Supporting Information

Selective Synthesis of Phenanthrenes and Dihydrophenanthrenes via Gold-Catalyzed Cycloisomerization of Biphenyl Embedded Trienynes

Ana Milián,[†] Patricia García-García,*[†] Adrián Pérez-Redondo,[†] Roberto Sanz,[‡] Juan J. Vaquero,[†] and Manuel A. Fernández-Rodríguez,*[†]

[†]Departamento de Química Orgánica y Química Inorgánica, Instituto de Investigación Química "Andrés M. del Río" (IQAR). Universidad de Alcalá (IRYCIS). Campus Científico-Tecnológico, Facultad de Farmacia. Autovía A-II, Km 33.1, 28805-Alcalá de Henares, Madrid, Spain.

[‡]Área de Química Orgánica. Departamento de Química, Facultad de Ciencias, Universidad de Burgos, Pza. Misael Bañuelos, s/n 09001, Burgos, Spain

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General Experimental Details

All reaction involving air sensitive compounds were carried out under inert atmosphere (Ar). Temperatures are reported as oil-bath temperatures. Dry solvents, where necessary, were dried by a MBRAUN MB-SPS-800 apparatus. Starting materials sourced from commercial suppliers were used as received unless otherwise stated. The following compounds: 1-bromo-2-(phenylethynyl)benzene,[1] 1-bromo-2-(hex-1-yn-1-yl)benzene,[2] (2-bromophenyl)ethynyltrimethylsilane,[3] (2-bromophenyl)ethynyltriisopropylsilane,[4] 2-bromo-4-chloro-1-(phenylethynyl)benzene,[5] 1-iodo-3,5-dimethoxybenzene,[6] 2-bromo-1-iodo-3,5-dimethoxybenzene,[7] 2'-(trimethylsilylethynyl)-[1,1'-biphenyl]-2-carbaldehyde[8] and 2-(prop-1-en-2-yl)phenylboronic acid[9] were prepared according to literature procedures. Reactions were monitored using analytical TLC plates (Merck; silica gel 60 F254, 0.25 mm), and compounds were visualized with UV radiation. Silica gel grade 60 (70-230 mesh, Merck) was used for column chromatography. All melting points were determined in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus (uncorrected). ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Mercury VX-300, Varian Unity 300 or Varian Unity 500 MHz spectrometer at room temperature. Chemical shifts are given in ppm (δ) downfield from tetramethylsilane, with calibration on the residual protio-solvent used (δ_H = 7.26 ppm and δ_C = 77.2 ppm for $CDCl_3$). Coupling constants (*J*) are in Hertz (Hz) and signals are described as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; bs, broad singlet; dd, double doublet; dq, double quadruplet; ddd, double doublet of doublets and m, multiplet. High-resolution analysis (HRMS) were performed on an Agilent 6210 time of-flight LC/MS.

[1] Verma, A. K.; Kesharwani, T.; Singh, J.; Tandon, V.; Larock, R. C. *Angew. Chem. Int. Ed.* **2009**, *48,* 1138-1143.
[2] Körner, C.; Starkov, P.; Sheppard, T. D. *J. Am. Chem. Soc.* **2010**, *132,* 5968-5969.
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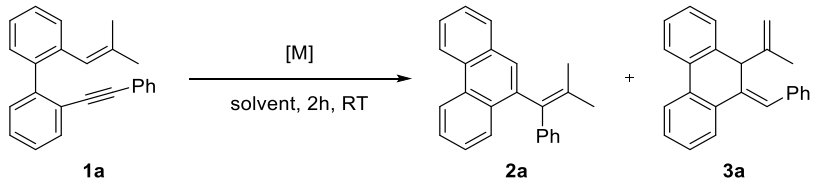
[5] Naveen, K.; Perumal, P. T.; Cho, D. *Org. Lett.* **2019**, *21,* 4350–4354.
[6] Guo, W.; Monge-Marcet, A.; Cattoen, X.; Shafir, A.; Pleixats, R. *Reactive & Functional Polymers.* **2013**, *73,* 192-199.
[7] Zysman-Colman, E.; Arias, K.; Siegel, J. S. *Can. J. Chem.* **2009**, *87*, 440–447.
[8] Debrouwer, W.; Furstner, A.; *Chem. Eur. J*. **2017**, *23*, 4271–4275.
[9] Benhamou, L.; Walker, D. W.; Bucar, D.; Aliev, A. E.; Sheppard, T. D. *Org. Biomol. Chem.* **2016**, *14*, 8039–8043.

Experimental Procedures and Data

Table S1. Cycloisomerization of 1a: Optimization of the Reaction Conditions.

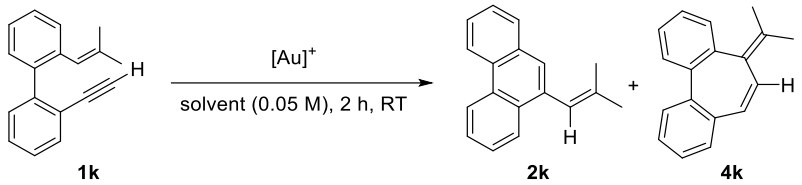


1a 2a 3a

Entry	[M]	mol%	Solvent	[M]	Conversion (yield)[a]	2a/3a
1	$AgNTf_2$	5	CH_2Cl_2	0.05	–	–
2	$Cu(OTf)_2$	5	CH_2Cl_2	0.05	–	–
3	$Pd(OAc)_2$	5	CH_2Cl_2	0.05	–	–
4	$ZnCl_2$	5	CH_2Cl_2	0.05	–	–
5	$InBr_3$	5	CH_2Cl_2	0.05	complex mixture	–
6	$PPh_3AuCl/AgNTf_2$	5	CH_2Cl_2	0.05	50	>95:<5
7	$PPh_3AuCl/AgOTf$	5	CH_2Cl_2	0.05	80	1:1
8	$PPh_3AuCl/AgOTs$	5	CH_2Cl_2	0.05	–	–
9	PPh_3AuNTf_2	5	CH_2Cl_2	0.05	100 (94%)	>95:<5
10	PPh_3AuNTf_2	5	Toluene	0.05	70	1:1
11	PPh_3AuNTf_2	5	DMF	0.05	–	–
12	PPh_3AuNTf_2	5	MeCN	0.05	–	–
13	PPh_3AuNTf_2	5	THF	0.05	25	<5:>95
14	$PPh_3AuCl/AgOTf$	5	THF	0.05	70	1:1.5
15[b]	PPh_3AuNTf_2	5	THF	0.05	100 (79%)	<5:>95
16	$(ArO_3P)AuCl/AgNTf_2$[c]	5	CH_2Cl_2	0.05	100	>90:<10
17	$t\text{-}Bu_3AuNTf_2$	5	CH_2Cl_2	0.05	80	>95:<5
18	$PEt_3AuCl/AgNTf_2$	5	CH_2Cl_2	0.05	100	94:6
19	$XPhosAuNTf_2$	5	CH_2Cl_2	0.05	100 (98)	94:6
20	$XPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.05	91	>95:<5
21	$JohnPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.05	100 (99)	>95:<5
22	$IPrAuCl/AgNTf_2$	5	CH_2Cl_2	0.05	100 (97)	>95:<5
23	$AuCl_3$	5	CH_2Cl_2	0.05	100 (98)	>95:<5
24	$IPrAuCl/AgNTf_2$	5	CH_2Cl_2	0.05	100 (97)	>95:<5
25	$JohnPhosAu(MeCN)SbF_6$	5	THF	0.05	100	1.6:1[d]
26	$JohnPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.005	100	94:6
27	$JohnPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.25	100	90:10
28	$JohnPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.05	100	>95:<5
29[e]	$JohnPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.05	100	>95:<5
30[f]	$JohnPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.05	100	90:10
31[g]	$JohnPhosAu(MeCN)SbF_6$	5	CH_2Cl_2	0.05	100	94:6
32[h]	$JohnPhosAu(MeCN)SbF_6$	1	CH_2Cl_2	0.05	100 (99)	>95:<5

[a] Conversion estimated by ^1H NMR (300 Hz); isolated yield in brackets for an experiment conducted with 0.2 mmol of **1a**. [b] Reaction conducted for 72 h. [c] Ar = 2,4-(tBu)$_2$C$_6$H$_4$. [d] Significant amounts of other unidentified products were also observed. [e] Conducted under argon. [f] Conducted in the presence of molecular sieves. [g] Performed at 70 ºC. [h] Conducted at 0 ºC

Table S2. Cycloisomerization of terminal substrate 1k: Optimization of the Reaction Conditions.



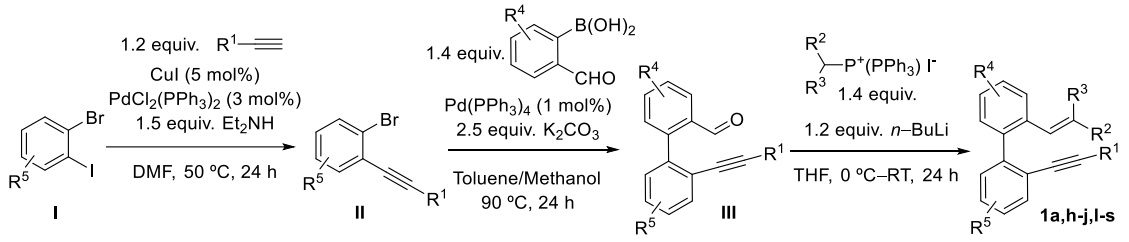
Entry	[M]	mol%	Solvent	Conversion (yield)[a]	2k/4k
1	PPh_3AuNTf_2	5	CH_2Cl_2	100	60/40
2	JackiePhosAuNTf$_2$	5	CH_2Cl_2	100	51/49
3	$(p\text{-}CF_3\text{-}C_6H_4)_3AuCl/AgNTf_2$	5	CH_2Cl_2	100	51/49
4	JohnPhosAu(MeCN)SbF$_6$	5	CH_2Cl_2	100	45/55
5	IPrAuCl/AgNTf$_2$	5	CH_2Cl_2	100	92/8
6	[{Au(IPr)}$_2$(μ-OH)][BF$_4$]	5	CH_2Cl_2	100	87/13
7	$AuCl_3$	5	CH_2Cl_2	100	100/0
8	$PPh_3AuCl/AgNTf_2$	5	CH_2Cl_2	100	67/33
9	$PPh_3AuCl/AgOTf$	5	CH_2Cl_2	100	67/33
10	$PPh_3AuCl/AgSbF_6$	5	CH_2Cl_2	100	68/32
11	$PPh_3AuCl/AgBF_4$	5	CH_2Cl_2	100	63/37
12	PPh_3AuNTf_2	5	THF	100	57/43
13[b]	PPh_3AuNTf_2	5	CH_3CN	65	28/37
14[c]	PPh_3AuNTf_2	5	Toluene	100	48/52
15	PPh_3AuNTf_2	5	CH_2Cl_2	100	70/30
16[d]	PPh_3AuNTf_2	5	1,2-DCE	100	64/36
17[d,e]	JohnPhosAu(MeCN)SbF$_6$	1	CH_2Cl_2	100	45/55
18[d,f]	JohnPhosAu(MeCN)SbF$_6$	1	CH_3CN	100	40/60
19	JohnPhosAu(MeCN)SbF$_6$	1	CH_3CN	100	42/58
20	JohnPhosAu(MeCN)SbF$_6$	1	CH_3CN	100	40/60

[a] Conversion estimated by ^{1}H NMR (300 Hz). [b] Conducted at 0 ºC. [c] Performed at 60 ºC. [d] Reaction conducted for 5 h. [e] Conducted under argon. [f] Conducted in the presence of molecular sieves.

General procedures for the synthesis of 2-alkenyl-2'-alkynyl-1,1'-biphenyls 1:

The starting substrates **1** were prepared following two protocols (Method A and B).

Method A: It involves a Sonogashira and Suzuki couplings and a Wittig reaction.



Step1:[10] In a round bottom flask, the appropiate alkyne (1.2 equiv.) was added to a solution of the corresponding 1-bromo-2-iodobenzene **I** (1 equiv.), Et_2NH (1.5 equiv.), CuI (0.05 equiv.) and $PdCl_2(PPh_3)_2$ (0.3 equiv.) in anhydrous DMF (0.25 M). The resulting mixture was stirred under Ar atmosphere at 50 ºC until complete consumption of the starting iodobenzene **I**, as monitored by TLC. Water and CH_2Cl_2 were added to the cooler reaction mixture. The separated aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography using mixtures of hexane and ethyl acetate as eluent to obtain the corresponding o-alkynylbromobenzenes **II** (86-99% yields) which were used in the next step.

Step 2:[11] The appropriate boronic acid (1.4 equiv.), $Pd(PPh_3)_4$ (0.01 equiv.) and the corresponding o-alkynylbromobenzene **II** obtained in step 1 (1 equiv.) were suspended in toluene (0.5 M). Then methanol (5 mL) and K_2CO_3 (2.5 equiv.) were added and the mixture was stirred thoroughly under Ar atmosphere at 90 ºC. After completion of reaction, toluene was evaporated under reduced pressure and crude product was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, and solvent was removed under reduced pressure. The residue was purified by flash chromatography using mixtures of hexane and EtOAc as eluents to obtain the biphenylcarbaldehydes **III** (60-99% yields) which were used in the next step.

Step 3:[12] *n*-BuLi (1.2 equiv., 1.6 M in hexanes) was added to a solution of the appropriate phosphonium halide (1.4 equiv.) in THF (0.25 M) at 0 ºC and the resulting mixture was stirred under argon atmosphere for 2 h at RT. The mixture was cooled to 0 ºC, the corresponding carbonyl **III** derivative obtained in step 2 (1 equiv.) was added and the reaction stirred at RT until the aldehyde **III** was consumed as determined by TLC. The resulting mixture was quenched with water and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography

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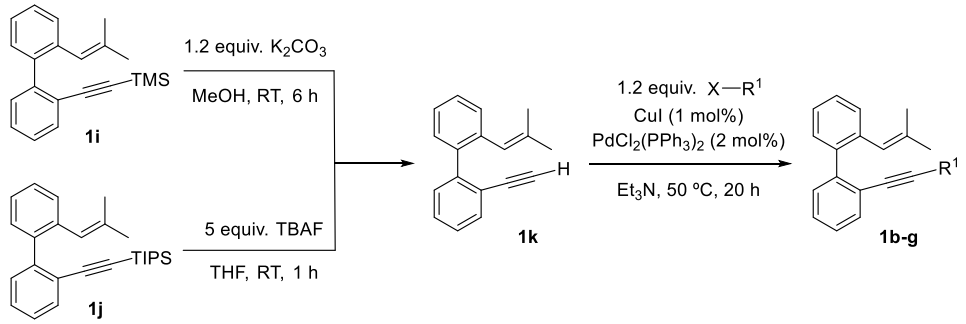
[12] Martínez, A.; García-García, P.; Fernández-Rodríguez, M. A.; Rodríguez, F.; Sanz, R. *Angew. Chem. Int. Ed.* **2010**, *49*, 4633–4637.

using mixtures of hexane and EtOAc as eluents to obtain the corresponding 2-alkenyl-2'-alkynyl-1,1'-biphenyls **1a,h-j,l-s** (50-99%).

Method B: It involves a deprotection step and a Sonogashira coupling from silyl derivatives **1i,j** obtained following step 3 of Method A from known 2'-(trimethylsilylethynyl)-[1,1'-biphenyl]-2-carbaldehyde[8] or the corresponding triisopropylsilyl derivative prepared using the same described procedure.



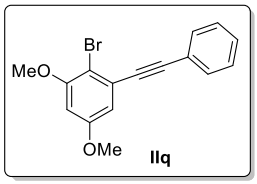
Step 1: The deprotection step could carry out in two different ways:

- ***Option 1.A:*** 2-(2-Methylprop-1-en-1-yl)-2'-(trimethylsilylethynyl)-1,1'-biphenyl **1i** (1 equiv. 6.3 mmol),[8] was dissolved in MeOH (60 mL) and K_2CO_3 was added (1.2 equiv., 7.6 mmol) at RT. The reaction mixture was stirred for 6 hours at RT and quenched with water (50 mL). The solution was concentrated, extracted with EtOAc, and chromatographed on a silica gel column using hexane as eluent to give 2-ethynyl-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl **1k** (1.44 g, 6.2 mmol, 99%) as colorless oil.
- ***Option 1.B:*** 2-(2-Methylprop-1-en-1-yl)-2'-(triisopropylsilylethynyl)-1,1'-biphenyl **1j** (1 equiv., 4.4 mmol), synthesized as **1i**,[8] was dissolved in THF (40 mL) and TBAF was added (5 equiv., 22 mmol, 22 mL, 1.0 M in THF) at 0 ºC. The reaction mixture was stirred for 1 hour at RT and quenched with water (50 mL). The solution was concentrated, extracted with diethyl ether, and chromatographed on a silica column using hexane as eluent to give 2-ethynyl-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl **1k** (1.02 g, 4.4 mmol, 99%) as colorless oil.

Step 2: In a round bottom flask, the appropriate haloarene (1.2 equiv., 0.7 mmol) was added to a solution of **1k** (1 equiv., 0.6 mmol), CuI (0.01 equiv., 0.01 mmol), $PdCl_2(PPh_3)_2$ (0.02 equiv., 0.01 mmol) in anhydrous Et_3N (2.5 mL). The resulting mixture was stirred under Ar atmosphere at 50 ºC until complete consumption of the acetylene, as monitored by TLC. Water and CH_2Cl_2 were added to the cooler reaction mixture. The separated aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography using mixtures of hexane and EtOAc as eluents to obtain the corresponding 2-alkenyl-2'-alkynyl-1,1'-biphenyls **1b-g**(89-99%).

Characterization data of biphenyl embedded trienynes 1 and intermediates II-III involved in their preparation.

2-Bromo-1,5-dimethoxy-3-(phenylethynyl)benzene (IIq)



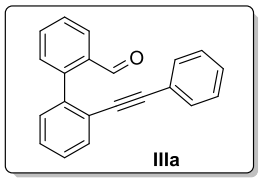
Obtained as a colorless oil (942 mg, 2.97 mmol, 94%) following the general procedure outlined above using compound **Iq** (1.08 g, 3.15 mmol). R_f = 0.48 (Hexane/EtOAc 9:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.63−7.60 (m, 2H), 7.37−7.35 (m, 3H), 6.73 (d, *J* = 2.7 Hz, 1H), 6.44 (d, *J* = 2.7 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.2 (C), 156.7 (C), 131.6 (2 x CH), 128.6 (CH), 128.3 (2 x CH), 126.3 (C), 122.7 (C), 108.6 (CH), 106.3 (C), 100.4 (CH), 93.6 (C), 88.4 (C), 56.3 (CH_3), 55.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrO_2$ 317.0172; Found 317.0170.

2'-(Phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (IIIa)



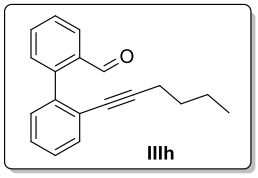
Obtained as a red oil (2.62 g, 9.28 mmol, 93%) following the general procedure outlined above using compound **IIa** (2.57 g, 10 mmol). R_f = 0.18 (Hexane/EtOAc 40:1)

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 9.90 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.62−7.59 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.41−7.37 (m, 3H), 7.36−7.34 (m, 1H), 7.21−7.16 (m, 3H), 7.14−7.11 (m, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 191.9 (CH), 144.4 (C), 140.4 (C), 134.3 (C), 133.6 (CH), 132.1 (CH), 131.4 (2 x CH), 130.3 (CH), 128.5 (2 x CH), 128.34 (2 x CH), 128.32 (3 x CH), 127.0 (CH), 123.8 (C), 122.8 (C), 93.9 (C), 88.3 (C).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}O$ 283.1117; Found 283.1108.

2'-(Hex-1-yn-1-yl)-[1,1'-biphenyl]-2-carbaldehyde (IIIh)



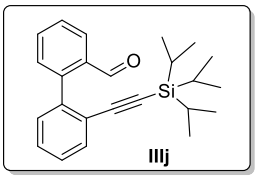
Obtained as a yellow oil (1.73 g, 6.59 mmol, 66%) following the general procedure outlined above using compound **IIh** (2.37 g, 10 mmol). R_f = 0.40 (Hexane/EtOAc 40:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.85 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.52−7.46 (m, 2H), 7.39−7.31 (m, 4H), 2.16 (t, *J* = 6.8 Hz, 2H), 1.31−1.23 (m, 2H), 1.18−1.05 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 192.1 (CH), 144.8 (C), 140.2 (C), 134.2 (C), 133.5 (CH), 132.1 (CH), 131.2 (CH), 130.2 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 126.9 (CH), 124.6 (C), 95.5 (C), 79.5 (C), 30.2 (CH_2), 21.7 (CH_2), 19.1 (CH_2), 13.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}O$ 263.1430; Found 263.1432.

Synthesis of 2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (IIIj)



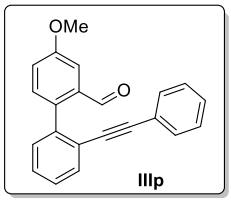
Obtained as an orange oil (3.08 mg, 8.49 mmol, 91%) from compound **IIj** (1 equiv., 9.34 mmol, 3.15 g) following the same described procedure for TMS derivative **IIIi**.[8] R_f = 0.33 (Hexane)

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.87 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.40–7.35 (m, 3H), 7.32–7.28 (m, 1H), 0.93 (s, 21H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 191.9 (CH), 144.6 (C), 140.6 (C), 134.0 (C), 133.4 (CH), 132.7 (CH), 131.0 (CH), 130.1 (CH), 128.3 (CH), 128.03 (CH), 127.97 (CH), 127.0 (CH), 123.9 (C), 105.2 (C), 95.8 (C), 18.7 (6 x CH_3), 11.3 (3 x CH).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}OSiNa$ 385.1958; Found 385.1951.

4-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (IIIp)



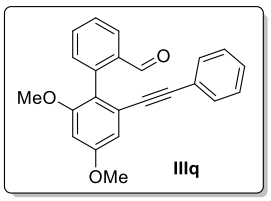
Obtained as an orange solid (443 mg, 1.42 mmol, 77%) following the general procedure outlined above using compound **IIa** (474 mg, 1.84 mmol). R_f = 0.18 (Hexane/EtOAc 40:1). M.p.: 55–56 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.91 (s, 1H), 7.66–7.62 (m, 1H), 7.59 (d, *J* = 2.8 Hz, 1H), 7.42–7.36 (m, 4H), 7.26-7.22 (m, 6H), 3.91 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 191.5 (CH), 159.4 (C), 139.9 (C), 137.2 (C), 135.1 (C), 132.6 (CH), 132.1 (CH), 131.3 (2 x CH), 130.6 (CH), 128.4 (2 x CH), 128.3 (2 x CH), 128.0 (CH), 123.9 (C), 122.8 (C), 120.9 (CH), 109.6 (CH), 93.7 (C), 88.5 (C), 55.8 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}O_2$ 313.1223; Found 313.1219.

2',4'-Dimethoxy-6'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (IIIq)



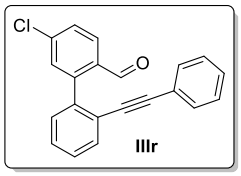
Obtained as a red oil (776 mg, 2.27 mmol, 76%) following the general procedure outlined above using compound **IIq** (942 mg, 2.97 mmol). R_f = 0.19 (Hexane/EtOAc 40:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.83 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.25−7.22 (m, 3H), 7.15−7.11 (m, 2H), 6.82 (d, *J* = 2.3 Hz, 1H), 6.58 (d, *J* = 2.3 Hz, 1H), 3.89 (s, 3H), 3.72 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 192.6 (CH), 160.5 (C), 158.0 (C), 140.5 (C), 134.8 (C), 133.3 (CH), 132.7 (CH), 131.4 (2 x CH), 128.5 (CH), 128.3 (2 x CH), 127.9 (CH), 126.7 (CH), 125.3 (C), 122.8 (C), 122.0 (C), 107.7 (CH), 99.7 (CH), 93.6 (C), 88.5 (C), 55.8 (CH_3), 55.7 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O_3$ 343.1329; Found 343.1334.

5-Chloro-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (IIIr)



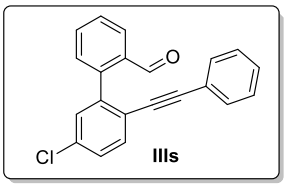
Obtained as a yellow oil (89 mg, 0.28 mmol, 97%) following the general procedure outlined above using compound **IIa** (75 mg, 0.29 mmol). R_f = 0.25 (Hexane/EtOAc 40:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.93 (s, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.71−7.63 (m, 1H), 7.54−7.36 (m, 6H), 7.27 (s, 4H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 190.6 (CH), 145.7 (C), 139.7 (C), 138.7 (C), 132.7 (C), 132.2 (CH), 131.4 (2 x CH), 131.3 (CH), 130.2 (CH), 128.8 (CH), 128.69 (CH), 128.66 (2 x CH), 128.5 (CH), 128.4 (2 x CH), 123.7 (C), 122.5 (C), 94.3 (C), 87.8 (C).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}OCl$ 317.0728; Found 317.0726.

5'-Chloro-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (IIIs)



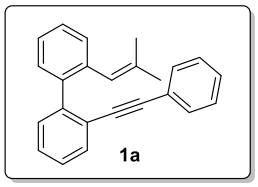
Obtained as a yellow oil (522 mg, 1.65 mmol, 66%) following the general procedure outlined above using compound **IIs** (731 mg, 2.50 mmol). R_f = 0.36 (Hexane/EtOAc 40:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.97 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.60−7.56 (m, 2H), 7.43-7.39 (m, 3H), 7.27−7.22 (m, 3H), 7.19−7.15 (m, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 191.2 (CH), 142.7 (C), 142.0 (C), 134.4 (C), 134.1 (C), 133.7 (CH), 133.0 (CH), 131.3 (2 x CH), 131.1 (CH), 130.1 (CH), 128.72 (CH), 128.66 (CH), 128.5 (CH), 128.3 (2 x CH), 127.2 (CH), 122.3 (2 x C), 94.7 (C), 87.2 (C).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}OCl$ 317.0728; Found 317.0731.

2-(2-Methylprop-1-en-1-yl)-2'-(phenylethynyl)-1,1'-biphenyl (1a)



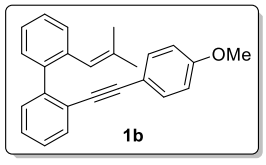
Obtained as white solid (2.39 g, 7.75 mmol, 75%) from **IIIa** (2.92 g, 10.34 mmol) following method A. R_f = 0.20 (Hexane). M.p.: 40−42 ºC.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.70−7.67 (m, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.44−7.42 (m, 2H), 7.40−7.32 (m, 5H), 7.29−7.25 (m, 4H), 6.16 (s, 1H), 1.78 (s, 3H), 1.76 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.4 (C), 140.2 (C), 137.5 (C), 135.0 (C), 131.8 (CH), 131.3 (2 x CH), 130.22 (CH), 130.18 (CH), 129.6 (CH), 128.1 (2 x CH), 127.9 (CH), 127.7 (CH), 127.1 (CH), 126.8 (CH), 125.7 (CH), 124.4 (CH), 123.5 (C), 122.8 (C), 92.4 (C), 89.4 (C), 26.4 (CH_3), 19.7 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}$ 309.1638; Found 309.1631.

2-(4-Methoxyphenylethynyl)-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl (1b)



Obtained as yellow oil (166 mg, 0.49 mmol, 98%) from **1k** (116 mg, 0.50 mmol) following method B. R_f = 0.31 (Hexane/EtOAc 40:1).

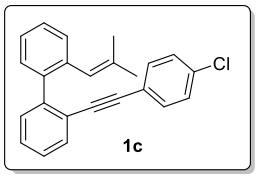
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.63−7.58 (m, 1H), 7.43

(d, *J* = 7.1 Hz, 1H), 7.40−7.25 (m, 6H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.06 (s, 1H), 3.79 (s, 3H), 1.76 (s, 3H), 1.72 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.5 (C), 144.2 (C), 140.5 (C), 137.7 (C), 135.1 (C), 132.9 (2 x CH), 131.7 (CH), 130.4 (CH), 130.3 (CH), 129.7 (CH), 127.4 (CH), 127.1 (CH), 126.9 (CH), 125.7 (CH), 124.5 (CH), 123.2 (C), 115.8 (C), 113.9 (2 x CH), 92.4 (C), 88.1 (C), 55.3 (CH_3), 26.3 (CH_3), 19.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1749.

2-(4-Chlorophenylethynyl)-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl (1c)



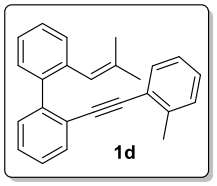
Obtained as colorless oil (133 mg, 0.39 mmol, 97%) from **1k** (93 mg, 0.40 mmol) following method B. R_f = 0.20 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50−7.44 (m, 1H), 7.28−7.13 (m, 7H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.89 (s, 1H), 1.59 (s, 3H), 1.55 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 144.6 (C), 140.3 (C), 137.7 (C), 135.3 (C), 134.0 (C), 132.6 (2 x CH), 131.9 (CH), 130.31 (CH), 130.28 (CH), 129.7 (CH), 128.6 (2 x CH), 128.0 (CH), 127.2 (CH), 127.0 (CH), 125.8 (CH), 124.4 (CH), 122.6 (C), 122.1 (C), 91.3 (C), 90.4 (C), 26.3 (CH_3), 19.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1240.

2-(2-Methylprop-1-en-1-yl)-2'-(o-tolylethynyl)-1,1'-biphenyl (1d)



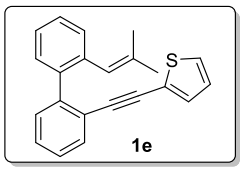
Obtained as yellow oil (155 mg, 0.48 mmol, 96%) from **1k** (116 mg, 0.50 mmol) following method B. R_f = 0.29 (Hexane/EtOAc 80:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.70−7.63 (m, 1H), 7.43−7.24 (m, 8H), 7.22−7.06 (m, 3H), 6.07 (s, 1H), 2.07 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 144.3 (C), 140.6 (C), 140.2 (C), 137.5 (C), 135.2 (C), 132.2 (CH), 131.9 (CH), 130.3 (CH), 130.2 (CH), 129.8 (CH), 129.4 (CH), 128.1 (CH), 127.7 (CH), 127.2 (CH), 126.9 (CH), 125.9 (CH), 125.4 (CH), 124.5 (CH), 123.4 (C), 123.2 (C), 93.1 (C), 91.3 (C), 26.3 (CH_3), 20.3 (CH_3), 19.5 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}$ 323.1794; Found 323.1796.

2-(2-Methylprop-1-en-1-yl)-2'-(thiophen-2-ylethynyl)-1,1'-biphenyl (1e)



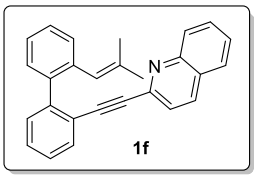
Obtained as yellow oil (160 mg, 0.51 mmol, 85%) from **1k** (139 mg, 0.60 mmol) following method B. R_f = 0.27 (Hexane).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.44 (d, *J* = 7.3 Hz, 1H), 7.27−7.11 (m, 7H), 7.02 (d, *J* = 5.2 Hz, 1H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.77−6.73 (m, 1H), 5.90 (s, 1H), 1.59 (s, 3H), 1.56 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.2 (C), 140.1 (C), 137.6 (C), 135.2 (C), 131.7 (CH), 131.5 (CH), 130.4 (CH), 130.2 (CH), 129.7 (CH), 127.9 (CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 125.8 (CH), 124.4 (CH), 123.7 (C), 122.7 (C), 93.2 (C), 85.5 (C), 26.3 (CH_3), 19.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}S$ 315.1202; Found 315.1201.

2-(2-Methylprop-1-en-1-yl)-2'-(quinolin-2-ylethynyl)-1,1'-biphenyl (1f)



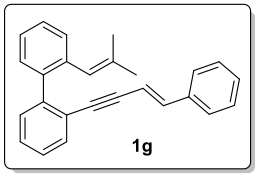
Obtained as yellow oil (203 mg, 0.56 mmol, 94%) from **1k** (139 mg, 0.60 mmol) following method B. R_f = 0.42 (Hexane/EtOAc 9:1).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.69−7.64 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.40−7.27 (m, 6H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.05 (s, 1H), 1.70 (s, 3H), 1.66 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 148.0 (C), 145.2 (C), 143.8 (C), 140.0 (C), 137.7 (C), 135.8 (CH), 135.4 (C), 132.6 (CH), 130.24 (CH), 130.20 (CH), 129.9 (CH), 129.7 (CH), 129.2 (CH), 128.7 (CH), 127.4 (CH), 127.2 (CH), 127.0 (CH), 126.89 (C), 126.88 (CH), 125.7 (CH), 124.5 (CH), 124.2 (CH), 121.7 (C), 92.2 (C), 90.3 (C), 26.2 (CH_3), 19.5 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}N$ 360.1747; Found 360.1750.

(*E*)-2-(2-Methylprop-1-en-1-yl)-2'-(4-phenylbut-3-en-1-yn-1-yl)-1,1'-biphenyl (1g)



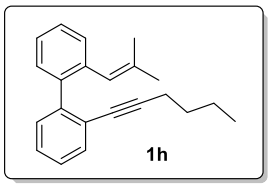
Obtained as yellow oil (178 mg, 0.53 mmol, 89%) from **1k** (139 mg, 0.60 mmol) following method B. R_f = 0.20 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.63−7.57 (m, 1H), 7.44−7.24 (m, 12H), 6.72 (d, *J* = 16.2 Hz, 1H), 6.21 (d, *J* = 16.2 Hz, 1H), 6.06 (s, 1H), 1.79 (bs, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 144.2 (C), 141.0 (CH), 140.2 (C), 137.6 (C), 136.4 (C), 135.1 (C), 132.0 (CH), 130.3 (CH), 130.2 (CH), 129.6 (CH), 128.7 (2 x CH), 128.5 (CH), 127.7 (CH), 127.1 (CH), 126.9 (CH), 126.2 (2 x CH), 125.7 (CH), 124.4 (CH), 123.0 (C), 108.5 (CH), 91.8 (C), 91.7 (C), 26.2 (CH_3), 19.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}$ 335.1794; Found 335.1790.

2-(Hex-1-yn-1-yl)-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl (1h)



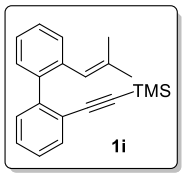
Obtained as yellow oil (482 mg, 1.67 mmol, 63%) from **IIIh** (691 mg, 2.63 mmol) following method A. R_f = 0.23 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.64−7.57 (m, 1H), 7.48−7.41 (m, 3H), 7.40−7.28 (m, 4H), 6.16 (s, 1H), 2.33 (t, *J* = 6.9 Hz, 2H), 1.85 (s, 6H), 1.52−1.40 (m, 2H), 1.39−1.25 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 144.2 (C), 140.6 (C), 137.4 (C), 134.7 (C), 132.1 (CH), 130.17 (CH), 130.15 (CH), 129.5 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 125.7 (CH), 124.7 (CH), 123.6 (C), 93.2 (C), 80.2 (C), 30.6 (CH_2), 26.2 (CH_3), 21.7 (CH_2), 19.5 (CH_3), 19.2 (CH_2), 13.7 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}$ 289.1951; Found 289.1951.

2-(2-Methylprop-1-en-1-yl)-2'-(trimethylsilylethynyl)-1,1'-biphenyl (1i)



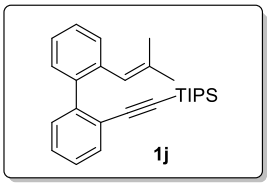
Obtained as colorless oil (2.10 g, 6.90 mmol, 78%) from **IIIi** (2.45 g, 8.80 mmol) following method A. R_f = 0.27 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 7.4 Hz, 1H), 7.28−7.13 (m, 7H), 5.97 (s, 1H), 1.66 (s, 3H), 1.64 (s, 3H), 0.00 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 145.1 (C), 140.2 (C), 137.4 (CH), 134.19 (C), 132.2 (CH), 130.2 (2 x CH), 129.6 (CH), 128.0 (CH), 127.1 (C), 126.7 (CH), 125.7 (CH), 124.6 (CH), 122.7 (C), 104.8 (C), 97.4 (C), 26.3 (CH_3), 19.6 (CH_3), 0.2 (3 x CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}Si$ 305.1720; Found 305.1717.

2-(2-Methylprop-1-en-1-yl)-2'-(triisopropylsilylethynyl)-1,1'-biphenyl (1j)



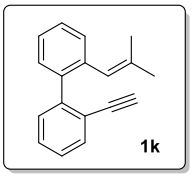
Obtained as colorless oil (2.81 g, 7.23 mmol, 78%) from **IIIj** (3.36 g, 9.27 mmol) following method A. R_f = 0.39 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.69 (d, *J* = 6.9 Hz, 1H), 7.46 (d, *J* = 6.9 Hz, 1H), 7.42−7.26 (m, 6H), 6.23 (s, 1H), 1.84 (s, 3H), 1.81 (s, 3H), 1.18−1.01 (m, 3H), 1.13 (s, 18H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 144.9 (C), 140.5 (C), 137.3 (C), 134.7 (C), 132.9 (CH), 130.4 (2 x CH), 129.7 (CH), 127.7 (CH), 127.1 (CH), 126.7 (CH), 125.9 (CH), 124.8 (CH), 123.0 (C), 106.6 (C), 93.4 (C), 26.3 (CH_3), 19.6 (CH_3), 18.7 (6 x CH_3), 11.4 (3 x CH).

HRMS (ESI-TOF) m/z: $[M+H-C_9H_{20}Si]^+$ Calcd for $C_{18}H_{17}$ 233.1325; Found 233.1327.

2-Ethynyl-2'-(2-methylprop-1-en-1-yl)-1,1'-biphenyl (1k)



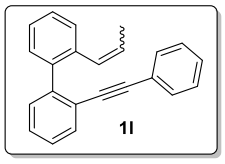
Obtained as colorless oil (1.44 g, 6.20 mmol, 98%) from **1i** or **1j** (6.30 mmol) following method B. R_f = 0.23 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46 (d, *J* = 7.5 Hz, 1H), 7.24−7.14 (m, 6H), 7.09 (d, *J* = 7.4 Hz, 1H), 5.85 (s, 1H), 2.80 (s, 1H), 1.62 (s, 3H), 1.61 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 144.8 (C), 140.0 (C), 137.6 (C), 135.3 (C), 133.1 (CH), 130.4 (CH), 130.1 (CH), 129.8 (CH), 128.3 (CH), 127.3 (CH), 126.9 (CH), 125.9 (CH), 124.5 (CH), 121.8 (C), 83.0 (C), 79.7 (CH), 26.3 (CH_3), 19.5 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd For $C_{18}H_{17}$ 233.1325; Found 233.1323.

2-(Phenylethynyl)-2'-(prop-1-en-1-yl)-1,1'-biphenyl (1l)



Mixture 2:1 of *Z*/*E* isomers (maj/min). Obtained as colorless oil (1.2 g, 4.08 mmol, 96%) from **IIIa** (1.2 g, 4.25 mmol) following method A. R_f = 0.25 (Hexane).

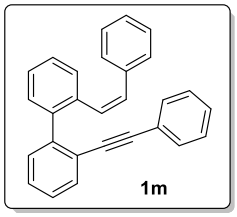
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.83−7.74 (m, 2H, maj + min), 7.62−7.55 (m, 2H, maj + min), 7.54−7.40 (m, 12H, maj + min), 7.31−7.38 (m, 10H, maj + min), 6.51−6.41 (m, 2H, maj + min), 6.31 (dq, *J* = 6.3, 12.7 Hz, 1H, min),

5.79 (dq, *J* = 7.1, 14.1 Hz, 1H, maj), 1.89 (d, *J* = 1.8 Hz, 3H, min), 1.87 (d, *J* = 1.8 Hz, 3H, maj).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 144.2 (C, maj), 144.0 (C, min), 140.5 (C, maj), 139.0 (C, min), 136.5 (C, min), 136.4 (C, maj), 131.91 (CH, maj), 131.88 (CH, min), 131.42 (2 x CH, maj), 131.40 (2 x CH, min), 130.6 (CH, min), 130.40 (CH, min), 130.36 (CH, maj), 130.2 (CH, maj), 129.5 (CH, min), 129.3 (2 x CH, maj + min), 129.2 (CH, maj), 128.20 (2 x CH, maj), 128.19 (2 x CH, min), 128.01(CH, maj), 127.98 (CH, min), 127.89 (CH, maj), 127.8 (CH, min), 127.14 (CH, min), 127.13 (CH, maj), 127.07 (CH, maj), 126.8 (CH, maj), 126.4 (CH, min), 126.3 (CH, maj), 126.2 (CH, min), 125.0 (CH, min) 123.53 (C, min) 123.51 (C, maj), 123.2 (C, min), 122.9 (C, maj), 92.9 (C, min) 92.6 (C, maj), 89.3 (C, maj), 89.2 (C, min), 18.8 (CH_3, min), 14.6 (CH_3, maj)

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}$ 295.1481; Found 295.1482.

(*Z*)-2-(Phenylethynyl)-2'-styryl-1,1'-biphenyl (1m)



Obtained as yellow oil (1.34 g, 3.76 mmol, 95%) from **IIIa** (1.12 g, 3.97 mmol) following method A. R_f = 0.14 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50−7.43 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.22−7.13 (m, 5H), 7.09−7.00 (m, 8H), 6.94−6.85 (m, 3H), 6.32 (d, *J* = 12.2 Hz, 1H), 6.27 (d, *J* = 12.2 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 143.8 (C), 140.4 (C), 137.0 (C), 136.5 (C), 132.0 (CH), 131.4 (2 x CH), 130.5 (CH), 130.3 (CH), 129.8 (CH), 129.7 (CH), 129.3 (CH), 129.0 (2 x CH), 128.2 (2 x CH), 128.04 (CH), 127.99 (2 x CH), 127.90 (CH), 127.4 (CH), 127.2 (CH), 126.9 (CH), 126.7 (CH), 123.4 (C), 122.8 (C), 92.8 (C), 89.4 (C).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{21}$ 357.1638; Found 357.1634.

Synthesis of (*Z*)-2-ethynyl-2'-(4-methoxystyryl)-1,1'-biphenyl (1n)

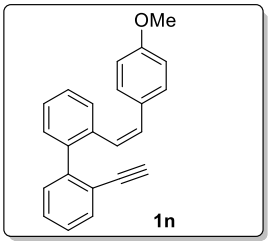
Following method A outlined above using compound **IIIn** (304 mg, 0.84 mmol), **TIPS-1n** was obtained as colorless oil (248 mg, 0.53 mmol, 63%). R_f = 0.20 (Hexane).

(*Z*)-2-(4-Methoxystyryl)-2'-(triisopropylsilylethynyl)-1,1'-biphenyl (TIPS-1n)

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.68−7.64 (m, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.35−7.28 (m, 4H), 7.25-7.22 (m, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.47 (d, *J* = 12.2 Hz, 1H), 6.40 (d, *J* = 12.2 Hz, 1H), 3.81 (s, 3H), 1.09 (s, 18H), 0.92−1.05 (m, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.6 (C), 144.1 (C), 140.3 (C), 136.6 (C), 133.0 (CH), 130.6 (CH), 130.3 (2 x CH), 130.2 (CH), 129.8 (C), 129.6 (CH), 129.4 (CH), 128.3 (CH), 127.9 (CH), 127.4 (CH), 127.0 (CH), 126.8 (CH), 122.7 (C), 113.5 (2 x CH), 106.2 (C), 93.9 (C), 55.2 (CH_3), 18.7 (6 x CH_3), 11.4 (3 x CH).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{32}H_{39}OSi$ 467.2765; Found 467.2751.



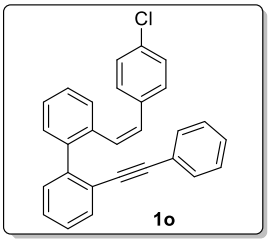
The subsequent deprotection of **TIPS-1n** (248 mg, 0.53 mmol) under the conditions described in method B afforded the title compound **1n** (95 mg, 0.31 mmol, 58%) as yellow oil. R_f = 0.45 (Hexane/EtOAc 20:1).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.25 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.99−6.86 (m, 5H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.38 (d, *J* = 7.2 Hz, 2H), 6.02 (d, *J* = 12.2 Hz, 1H), 5.93 (d, *J* = 12.2 Hz, 1H), 3.39 (s, 3H), 2.59 (s, 1H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 158.7 (C), 144.2 (C), 140.0 (C), 136.8 (C), 133.1 (CH), 130.34 (2 x CH), 130.33 (CH), 130.1 (CH), 129.7 (CH), 129.6 (C), 129.3 (CH), 128.4 (CH), 127.9 (CH), 127.5 (CH), 127.1 (CH), 126.8 (CH), 121.7 (C), 113.5 (2 x CH), 83.1 (C), 80.3 (CH), 55.2 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O$ 311.1430; Found 311.1432.

(Z)-2-(4-Chlorostyryl)-2'-(phenylethynyl)-1,1'-biphenyl (1o)



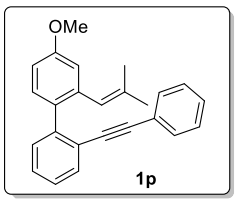
Obtained as yellow oil (244 mg, 0.62 mmol, 88%) from **IIIa** (200 mg, 0.71 mmol) following method A. R_f = 0.10 (Hexane).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.69−7.59 (m, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.43−7.18 (m, 11H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.51 (d, *J* = 12.2 Hz, 1H), 6.37 (d, *J* = 12.2 Hz, 1H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.8 (C), 140.5 (C), 136.3 (C), 135.5 (C), 132.6 (C), 132.1 (CH), 131.5 (2 x CH), 130.7 (CH), 130.5 (CH), 130.4 (2 x CH), 129.8 (CH), 129.24 (CH), 129.17 (CH), 128.4 (2 x CH), 128.3 (3 x CH), 128.0 (CH), 127.6 (CH), 127.3 (CH), 127.1 (CH), 123.4 (C), 122.9 (C), 92.8 (C), 89.3 (C).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{20}Cl$ 391.1248; Found 391.1250.

4-Methoxy-2-(2-methylprop-1-en-1-yl)-2'-(phenylethynyl)-1,1'-biphenyl (1p)



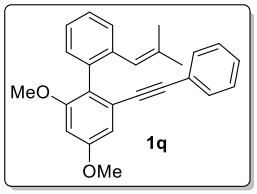
Obtained as yellow oil (251 mg, 0.74 mmol, 66%) from **IIIp** (351 mg, 1.12 mmol) following method A. R_f = 0.12 (Hexane/CH_2Cl_2 8:2).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.62 (d, *J* = 7.1 Hz, 1H), 7.42−7.30 (m, 3H), 7.27 (s, 6H), 6.93−6.86 (m, *2*H), 6.06 (s, 1H), 3.90 (s, 3H), 1.74 (s, 3H), 1.70 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.6 (C), 144.1 (C), 138.9 (C), 135.4 (C), 133.0 (C), 132.1 (CH), 131.5 (3 x CH), 130.8 (CH), 128.2 (2 x CH), 128.0 (CH), 127.7 (CH), 126.7 (CH), 124.6 (CH), 123.7 (C), 123.1 (C), 115.0 (CH), 111.2 (CH), 92.2 (C), 89.6 (C), 55.3 (CH_3), 26.2 (CH_3), 19.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1741.

2,4-Dimethoxy-2'-(2-methylprop-1-en-1-yl)-6-(phenylethynyl)-1,1'-biphenyl (1q)



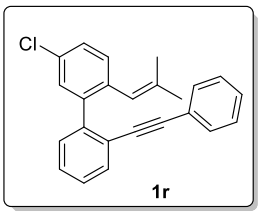
Obtained as orange solid (413 mg, 1.12 mmol, 49%) from **IIIq** (776 mg, 2.27 mmol) following method A. R_f = 0.13 (Hexane/EtOAc 40:1). M. p.: 76−78 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.38−7.31 (m, 4H), 7.27−7.21 (m, 3H), 7.17−7.10 (m, 2H), 6.79 (d, *J* = 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 5.99 (s, 1H), 3.89 (s, 3H), 3.71 (s, 3H), 1.73 (s, 3H), 1.70 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.5 (C), 157.9 (C), 139.0 (C), 136.6 (C), 134.6 (C), 131.5 (2 x CH), 131.0 (CH), 129.3 (CH), 128.2 (2 x CH), 128.0 (CH), 126.9 (CH), 126.8 (C), 125.7 (CH), 124.51 (C), 124.48 (CH), 123.4 (C), 107.0 (CH), 99.8 (CH), 92.3 (C), 89.3 (C), 55.7 (CH_3), 55.5 (CH_3), 26.2 (CH_3), 19.4 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1854.

5-Chloro-2-(2-methylprop-1-en-1-yl)-2'-(phenylethynyl)-1,1'-biphenyl (1r)



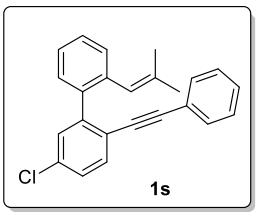
Obtained as colorless oil (87 mg, 0.25 mmol, 52%) from **IIIr** (155 mg, 0.49 mmol) following method A. R_f = 0.29 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.65−7.59 (m, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.38−7.31 (m, 3H), 7.31−7.21 (m, 7H), 5.95 (s, 1H), 1.71 (s, 3H), 1.66 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 142.9 (C), 141.8 (C), 136.2 (C), 136.0 (2 x C), 132.2 (CH), 131.5 (2 x CH), 131.2 (C), 131.0 (CH), 130.3 (CH), 130.2 (CH), 128.3 (2 x CH), 128.2 (CH), 127.9 (CH), 127.4 (CH), 127.2 (CH), 123.4 (CH), 122.8 (C), 92.9 (C), 88.9 (C), 26.3 (CH_3), 19.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1247.

5-Chloro-2'-(2-methylprop-1-en-1-yl)-2-(phenylethynyl)-1,1'-biphenyl (1s)



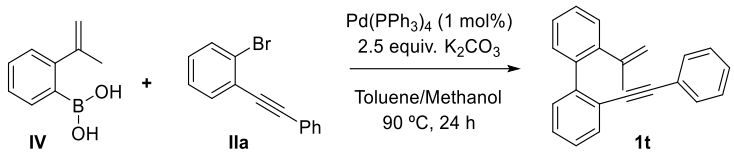
Obtained as yellow oil (357 mg, 1.04 mmol, 63%) from **IIIr** (522 mg, 1.65 mmol) following method A. R_f = 0.29 (Hexane).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.61 (d, *J* = 8.3 Hz, 1H), 7.50−7.43 (m, 3H), 7.43−7.35 (m, 3H), 7.34−7.26 (m, 5H), 6.17 (s, 1H), 1.84 (s, 3H), 1.78 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.1 (C), 139.0 (C), 137.6 (C), 135.8 (C), 133.6 (C), 133.0 (CH), 131.4 (2 x CH), 130.3 (CH), 130.0 (CH), 129.8 (CH), 128.3 (2 x CH), 128.2 (CH), 127.6 (CH), 127.2 (CH), 125.9 (CH), 124.1 (CH), 123.3 (C), 121.6 (C), 93.3 (C), 88.4 (C), 26.2 (CH_3), 19.6 (CH_3).

HRMS (ESI-TOF) calculated for $C_{24}H_{20}Cl$ $[M+H]^+$: 343.1248. Found $[M+H]^+$: 343.1248.

Synthesis of 2-(phenylethynyl)-2'-(prop-1-en-2-yl)-1,1'-biphenyl (1t)



Following the step 2 of Method A, (2-(prop-1-en-2-yl)phenyl)boronic acid **IV**[9] (1.4 equiv., 0.7 mmol, 113 mg), $Pd(PPh_3)_4$ (0.01 equiv., 0.005 mmol) and 1-bromo-2-ethynyl-benzene (1 equiv., 0.5 mmol, 128 mg) were suspended in toluene (4 mL). Then ethanol (1 mL) and K_2CO_3 (2.5 equiv., 1.25 mmol) were added and the mixture was stirred thoroughly under argon atmosphere at 90 °C. After 24 hours, toluene was evaporated under reduced pressure and the crude was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, and solvents were removed under reduced pressure. The residue was purified by flash chromatography using hexane as eluent to obtain 2-(phenylethynyl)-2'-(prop-1-en-2-yl)-1,1'-biphenyl **1t** (129 mg, 0.44 mmol, 88%) as colorless oil. R_f = 0.24 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.61−7.57 (m, 1H), 7.40−7.33 (m, 4H), 7.33−7.30 (m, 3H), 7.25 (d, *J* = 1.3 Hz, 1H), 7.24−7.22 (m, 2H), 7.19−7.14 (m, 2H), 5.00−4.97 (m, 1H), 4.86-4.84 (m, 1H), 1.77 (dd, *J* = 0.8 and 1.4 Hz, 3H).

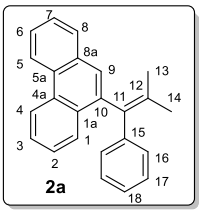
^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 145.5 (C), 144.9 (C), 143.4 (C), 138.7 (C), 132.0 (CH), 131.5 (2 x CH), 130.9 (CH), 130.1 (CH), 128.31 (CH), 128.30 (2 x CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 127.0 (CH), 126.5 (CH), 123.6 (C), 122.8 (C), 116.3 (CH_2), 92.8 (C), 89.5 (C), 23.7 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}$ 295.1481; Found 295.1471.

General procedure for the synthesis of phenanthrenes 2.

In a round bottom flask, JohnPhosAu(MeCN)SbF_6 (1 mol%, 3 mg) was added to a solution of the corresponding 2-alkenyl-2'-alkynyl-1,1'-biphenyl **1** (1 equiv., 0.4 mmol) in CH_2Cl_2 (8 mL, 0.05 M) and the reaction mixture was stirred for 2 h at RT. The resulting mixture was filtered over a plug of Celite eluting with a mixture of hexane/EtOAc 40:1 and solvents were removed under reduced pressure. The crude reaction mixture was purified by flash chromatography on silica gel using mixtures of hexane and EtOAc as eluents to give the corresponding phenanthrenes **2**.

9-(2-Methyl-1-phenylprop-1-en-1-yl)phenanthrene (2a)



Obtained as white solid (305 mg, 1 mmol, 99%) from **1a** (308 mg, 1 mmol). R_f = 0.20 (Hexane). M.p.: 191−193 °C.

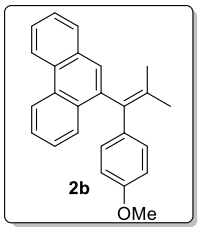
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.74 (d, *J* = 8.2 Hz, 1H, H-4), 8.70 (d, *J* = 8.1 Hz, 1H, H-5), 8.13 (d, *J* = 8.1 Hz, 1H, H-1), 7.88 (d, *J* = 7.7 Hz, 1H, H-8), 7.67−7.62 (m, 3H, H-3, H-6, H-9), 7.62−7.58 (m, 2H, H-2, H-7), 7.39−7.36 (m, 2H, H-17), 7.29−7.24 (m, 2H, H-16), 7.17 (t, *J* = 7.4 Hz, 1H, H-18), 2.08 (s, 3H, H-13/14), 1.67 (s, 3H, H-13/14).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 142.5 (C, C-15), 139.9 (C, C-10), 134.6 (C, C-11), 133.6 (C, C-12), 132.1 (C, C-8a), 131.4 (C, C-1a), 130.8 (C, C-4a), 129.9 (C, C-5a), 129.4 (2 x CH, C-16), 128.6 (CH, C-8), 128.0 (2 x CH, C-17), 127.7 (CH, C-9),

127.0 (CH, C-1), 126.8 (CH, C-2/7), 126.7 (CH, C-2/7), 126.4 (CH, C-18), 126.33 (CH, C-3/6), 126.29 (CH, C-3/6), 123.0 (CH, C-4), 122.6 (CH, C-5), 23.1 (CH_3, C-13/14), 22.1 (CH_3, C-13/14).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}$ 309.1638; Found 309.1630.

9-(1-(4-Methoxyphenyl)-2-methylprop-1-en-1-yl)phenanthrene (2b)



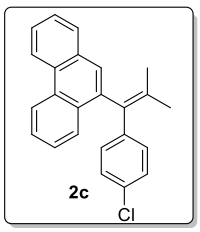
Obtained as yellow solid (135 mg, 0.39 mmol, 99%) from **1b** (135 mg). R_f = 0.25 (Hexane/EtOAc 40:1). M.p.: 154−156 ºC.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.75 (d, *J* = 8.1 Hz, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.68−7.58 (m, 5H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 2.10 (s, 3H), 1.68 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 158.0 (C), 140.1 (C), 135.0 (C), 134.1 (C), 132.8 (C), 132.1 (C), 131.4 (C), 130.8 (C), 130.5 (2 x CH), 129.9 (C), 128.6 (CH), 127.5 (CH), 127.0 (CH), 126.73 (CH), 126.67 (CH), 126.4 (CH), 126.3 (CH), 123.0 (CH), 122.6 (CH), 113.3 (2 x CH), 55.3 (CH_3), 23.1 (CH_3), 22.1 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1738.

9-(1-(4-Chlorophenyl)-2-methylprop-1-en-1-yl)phenanthrene (2c)



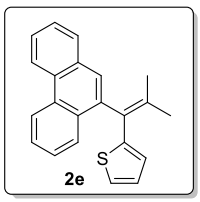
Obtained as white solid (136 mg, 99%) from **1c** (137 mg). R_f = 0.67 (Hexane). M.p.: 141−143 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.75 (d, *J* = 8.2 Hz, 1H), 8.71 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.71−7.57 (m, 5H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 2.07 (s, 3H), 1.69 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 140.9 (C), 139.4 (C), 134.4 (C), 133.6 (C), 132.03 (C), 131.95 (C), 131.2 (C), 130.9 (C), 130.7 (2 x CH), 130.0 (C), 128.6 (CH), 128.2 (2 x CH), 127.8 (CH), 126.84 (CH), 126.79 (CH), 126.73 (CH), 126.5 (2 x CH), 123.1 (CH), 122.6 (CH), 23.2 (CH_3), 22.1 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1237.

9-(1-(2-Thienyl)-2-methylprop-1-en-1-yl)phenanthrene (2e)



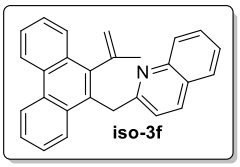
Obtained as yellow solid (105 mg, 0.33 mmol, 83%) from **1e** (126 mg). R_f = 0.20 (Hexane). M.p.: 177−180 ºC.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.74 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.69−7.59 (m, 4H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 5.1 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.86 (d, *J* = 3.5 Hz, 1H), 2.29 (s, 3H), 1.67 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 145.1 (C), 139.6 (C), 134.8 (C), 132.0 (C), 131.2 (C), 130.9 (C), 130.1 (C), 128.7 (CH), 128.2 (C), 127.4 (CH), 126.9 (CH), 126.74 (CH), 126.71 (CH), 126.6 (2 x CH), 126.54 (CH), 126.53 (CH), 124.5 (CH), 123.0 (CH), 122.7 (CH), 23.8 (CH_3), 22.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}S$ 315.1202; Found 315.1203.

9-(Prop-1-en-2-yl)-10-(quinolin-2-ylmethyl)phenanthrene (iso-3f)



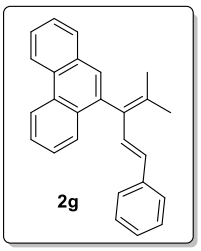
Obtained as red oil (104 mg, 72%) from **1f** (144 mg) after 24 h following the general procedure but in the presence of PTSA (1 equiv., 69 mg). R_f = 0.36 (Hexane/EtOAc 9:1).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.75 (m, 2H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.75 (t, *J* = 8.3 Hz, 1H), 7.72−7.65 (m, 3H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 5.55 (bs, 1H), 5.11 (bs, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 17.1 Hz, 1H), 2.20 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 162.1 (C), 144.0 (2 x C), 140.8 (C), 136.7 (CH), 131.4 (C), 130.4 (2 x C), 130.3 (C), 129.7 (CH), 128.7 (CH), 128.1 (C), 127.6 (CH), 127.1 (CH), 127.0 (CH), 126.9 (CH), 126.8 (C), 126.5 (CH), 126.24 (CH), 126.17 (CH), 126.0 (CH), 123.0 (CH), 122.8 (CH), 120.4 (CH), 117.4 (CH_2), 40.2 (CH_2), 25.3 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{22}N$ 360.1747; Found 360.1735.

(*E*)-9-(4-Methyl-1-phenylpenta-1,3-dien-3-yl)phenanthrene (2g)



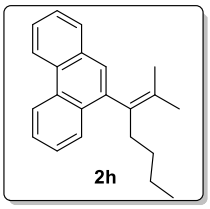
Obtained as colorless oil (94 mg, 0.28 mmol, 70%) from **1g** (134 mg). R_f = 0.14 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.78 (dd, *J* = 3.5, 8.2 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.72−7.61 (m, 4H), 7.57−7.52 (m, 2H), 7.27−7.20 (m, 4H), 7.17-7.10 (m, 1H), 5.85 (d, *J* = 15.9 Hz, 1H), 2.26 (s, 3H), 1.58 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 138.2 (C), 137.2 (C), 135.8 (C), 133.3 (C), 132.1 (C), 131.6 (C), 130.7 (C), 130.1 (C), 130.0 (CH), 128.7 (CH), 128.5 (2 x CH), 128.0 (CH), 127.9 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 126.3 (2 x CH), 122.9 (CH), 122.7 (CH), 23.6 (CH_3), 20.3 (CH_3).

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}Na$ 357.1614; Found 357.1599.

9-(2-Methylhept-2-en-3-yl)phenanthrene (2h)



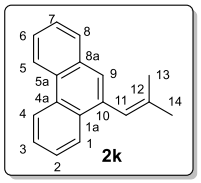
Obtained as colorless oil (93 mg, 0.32 mmol, 81%) from **1h** (115 mg). R_f = 0.36 (Hexane/EtOAc 40:1).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.78 (d, *J* = 8.2 Hz, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.72−7.60 (m, 4H), 7.50 (s, 1H), 2.71−2.63 (m, 1H), 2.39-2.30 (m, 1H), 2.03 (s, 3H), 1.52 (s, 3H), 1.46−1.31 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 140.5 (C), 133.3 (C), 132.1 (C), 131.4 (C), 130.7 (C), 129.7 (C), 129.5 (C), 128.5 (CH), 126.8 (CH), 126.6 (CH), 126.5 (CH), 126.33 (CH), 126.28 (CH), 126.1 (CH), 123.0 (CH), 122.6 (CH), 34.5 (CH_2), 30.9 (CH_2), 23.1 (CH_2), 22.5 (CH_3), 20.0 (CH_3), 14.2 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}$ 289.1951; Found 289.1952.

9-(2-Methylprop-1-en-1-yl)phenanthrene (2k)



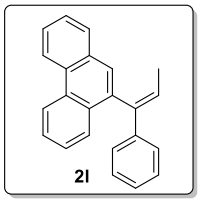
Obtained as white solid (88 mg, 0.38 mmol, 95%) from **1k** (93 mg) using $AuCl_3$ (5 mol%, 0.02 mmol, 6 mg) as catalyst. R_f = 0.38 (Hexane). M.p.: 77−79 ºC

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.74 (d, *J* = 8.0 Hz, 1H, H-4), 8.69 (d, *J* = 7.2 Hz, 1H, H-5), 8.10 (d, *J* = 7.7 Hz, 1H, H-1), 7.87 (d, *J* = 7.2 Hz, 1H, H-8), 7.71−7.58 (m, 4H, H-2, H-3, H-6, H-7), 7.56 (s, 1H, H-9), 6.68 (s, 1H, H-11), 2.08 (s, 3H, H-14), 1.80 (s, 3H, H-13).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 137.4 (C, C-12), 134.5 (C, C-4a), 131.9 (C, C-8a), 131.8 (C, C-1a), 130.5 (C, C-10), 129.8 (C, C-5a), 128.5 (CH, C-8), 127.3 (CH, C-9), 126.7 (CH, C-2/3/6/7), 126.5 (CH, C-2/3/6/7), 126.4 (CH, C-2/3/6/7), 126.2 (CH, C-2/3/6/7), 126.0 (CH, C-1), 123.2 (CH, C-11), 123.0 (CH, C-4), 122.6 (CH, C-5), 26.3 (CH_3,C-14), 19.8 (CH_3,C-13).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}$ 233.1325; Found 233.1320.

9-(1-Phenylprop-1-en-1-yl)phenanthrene (2l)



Obtained as white solid (2:1 *Z*:*E* mixture, 104 mg, 0.35 mmol, 88%) from **1l** (2:1 *Z*:*E* mixture, 118 mg). R_f = 0.24 (Hexane). M.p.: 127−129 ºC

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.82−8.74 (m, 2H, maj), 8.74−8.67 (m, 2H, min), 8.01 (d, *J* = 8.2 Hz, 1H, min), 7.95−7.89 (m, 2H maj + 1H min), 7.75−7.18 (m, 20H, maj + min), 6.64 (q, *J* = 6.9 Hz, 1H, maj), 6.14 (q, *J* = 7.1 Hz, 1H, min), 2.11 (d, *J* = 7.1 Hz, 3H min), 1.68 (d, *J* = 6.9 Hz, 3H maj).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 141.9 (C maj), 141.4 (C min), 140.9 (C min), 140.4 (C maj), 140.2 (C min), 136.2 (C maj), 132.0 (C maj), 131.9 (C min), 131.6 (C min), 131.3 (C maj), 130.8 (C maj), 130.5 (C min), 130.21 (C maj), 130.20 (C min), 129.4 (3 x CH min), 129.2 (CH min), 128.70 (CH maj), 128.69 (2 x CH min), 128.4 (2 x CH maj), 128.2 (CH maj), 128.0 (CH min), 127.7 (CH min), 127.4 (CH min), 127.0 (CH maj), 126.93 (CH min), 126.89 (2 x CH maj), 126.81 (CH maj + CH min), 126.62 (CH maj), 126.59 (CH maj), 126.50 (CH min), 126.48 (CH min), 126.3 (2 x CH maj), 126.0 (CH maj), 123.0 (CH maj), 122.9 (CH min), 122.7 (CH maj), 122.6 (CH min), 16.0 (CH_3 maj), 15.8 (CH_3 min).

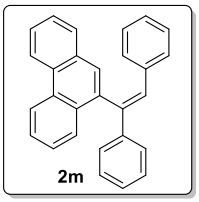
The major isomer could be isolated in almost pure form:

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.81−8.74 (m, 2H), 7.94−7.88 (m, *2*H), 7.74−7.64 (m, 4H), 7.56−7.49 (m, 1H), 7.38−7.34 (m, 2H), 7.29−7.20 (m, 3H), 6.64 (q, *J* = 6.9 Hz, 1H), 1.69 (d, *J* = 6.9 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 141.8 (C), 140.3 (C), 136.1 (C), 131.9 (C), 131.2 (C), 130.7 (C), 130.1 (C), 128.6 (CH), 128.3 (2 x CH), 128.1 (CH), 126.9 (CH), 126.8 (2 x CH), 126.7 (CH), 126.53 (CH), 126.50 (CH), 126.2 (2 x CH), 125.9 (CH), 122.9 (CH), 122.6 (CH), 16.1 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}$ 295.1481; Found 295.1479.

(Z)-9-(1,2-diphenylvinyl)phenanthrene (2m)



Obtained as white solid (*Z*:*E* > 10:1, 140 mg, 0.39 mmol, 98%) from **1m** (*Z*:*E* > 10:1, 143 mg). R_f = 0.20 (Hexane). M.p.: 146−148 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.79 (d, *J* = 4.5 Hz, 1H), 8.76 (d, *J* = 4.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.73-7.57 (m, 4H), 7.49-7.41 (m, 3H), 7.40 (s, 1H), 7.29-7.24 (m, 3H), 7.06-6.97 (m, 5H).

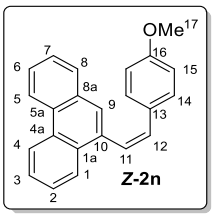
^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 142.8 (C), 140.3 (C), 137.0 (C), 136.6 (C), 132.1 (C), 131.1 (C), 131.0 (C), 130.4 (C), 130.3 (CH), 129.3 (2 x CH), 129.0 (CH), 128.6 (2 x CH), 128.4 (CH), 128.3 (2 x CH), 127.7 (CH), 127.1 (2 x CH), 127.0 (CH), 126.9 (2 x CH), 126.8 (CH), 126.7 (2 x CH), 123.1 (CH), 122.7 (CH).

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{20}Na$ 379.1457; Found 379.1460.

9-(4-Methoxystyryl)phenanthrene (2n)

Obtained as a 4:1 mixture of *Z*:*E*, of *Z*/*E* isomers (maj/min) (119 mg, 0.38 mmol, 96%) from **1n** (*Z*:*E* > 10:1, 124 mg). The isomers could be separated.

(*Z*)-9-(4-methoxystyryl)phenanthrene (maj):



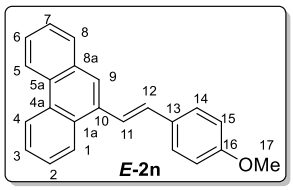
White solid. R_f = 0.23 (Hexane/CH_2Cl_2 9:1). M.p.: 121−123 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.77 (d, *J* = 8.2 Hz, 1H, H-4), 8.71 (d, *J* = 8.2 Hz, 1H, H-5), 8.20 (d, *J* = 8.0 Hz, 1H, H-1), 7.75 (d, *J* = 7.8 Hz, 1H, H-8), 7.72−7.68 (m, 2H, H-3, H-9), 7.66−7.58 (m, 2H, H-2, H-6), 7.58–7.54 (m, 1H, H-7), 7.12 (d, *J* = 8.8 Hz, 2H, H-14), 6.94 (d, *J* = 12.2 Hz, 1H, H-11), 6.84 (d, *J* = 12.2 Hz, 1H, H-12), 6.60 (d, *J* = 8.9 Hz, 2H, H-15), 3.68 (s, 3H, H-17).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.8 (C, C-16), 134.5 (C, C-10), 132.0 (C, C-8a), 131.9 (CH, C-12), 131.0 (C, C-1a), 130.7 (C, C-4a), 130.5 (2 x CH, C-14), 130.1 (C, C-5a), 129.4 (C, C-13), 128.7 (CH, C-8), 126.84 (2 x CH, C-2/6/9), 126.81 (CH ,C-2/6/9), 126.7 (CH, C-3/7), 126.57 (CH, C-3/7), 126.55 (CH, C-11), 125.9 (CH, C-1), 123.1 (CH, C-4), 122.6 (CH, C-5), 113.7 (2 x CH, C-15), 55.2 (CH_3, C-17).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O$ 311.1430; Found 311.1436.

(*E*)-9-(4-Methoxystyryl)phenanthrene (min):



Yellow solid. R_f = 0.17 (Hexane/CH_2Cl_2 9:1). M.p.: 198−200 ºC.

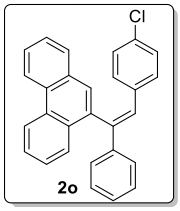
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.74 (d, *J* = 8.0 Hz, 1H, H-4), 8.66 (d, *J* = 8.0 Hz, 1H, H-5), 8.26 (d, *J* = 7.7 Hz, 1H, H-1), 7.94 (s, 1H, H-9), 7.90 (d, *J* = 7.5 Hz, 1H, H-8), 7.73 (d, *J* = 15.9 Hz, 1H, H-11), 7.71−7.59 (m, 4H, H-2/3/6/7), 7.57 (d, *J* = 8.7 Hz, 2H, H-14), 7.18 (d, *J* = 15.9 Hz, 1H, H-12), 6.95 (d, *J* = 8.7 Hz, 2H, H-15), 3.86 (s, 3H, H-17).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 159.6 (C, C-16), 134.4 (C, C-10), 132.1 (C, C-8a), 131.8 (CH, C-12), 131.0 (C, C-1a), 130.6 (2 x C, C-4a, C-13), 130.3 (C, C-5a), 128.8 (CH, C-8), 128.1 (2 x CH, C-14), 126.9 (CH C-2/3/6/7), 126.8 (CH C-2/3/6/7), 126.6 (CH C-2/3/6/7), 126.5 (CH, C-2/3/6/7), 124.8 (CH, C-1), 124.34 (CH, C-9/11),

124.31 (CH, C-9/11), 123.26 (CH, C-4), 122.7 (CH, C-5), 114.4 (2 x CH, C-15), 55.5 (CH_3, C-17).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O$ 311.1430; Found 311.1440.

(*Z*)-9-(2-(4-Chlorophenyl)-1-phenylvinyl)phenanthrene (2o)



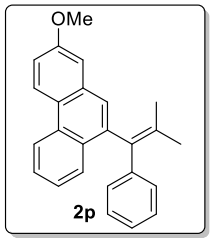
Obtained as yellow oil (*Z*:*E* > 10:1, 129 mg, 0.33 mmol, 83%) from **1o** (*Z*:*E* > 10:1, 156 mg). R_f = 0.17 (Hexane/EtOAc 40:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.79 (dd, *J* = 7.8, 6.0 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.77−7.59 (m, 4H), 7.52−7.43 (m, 3H), 7.36 (s, 1H), 7.33−7.25 (m, 3H), 6.96 (s, 4H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 142.5 (C), 141.1 (C), 136.2 (C), 135.5 (C), 132.7 (C), 131.9 (C), 131.0 (C), 130.9 (C), 130.43 (2 x CH), 130.39 (C), 128.93 (CH), 128.85 (CH), 128.6 (2 x CH), 128.5 (CH), 128.4 (2 x CH), 127.9 (CH), 127.2 (CH), 127.02 (CH), 126.96 (CH), 126.93 (CH), 126.8 (CH), 126.7 (2 x CH), 123.2 (CH), 122.8 (CH).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{20}Cl$ 391.1248; Found 391.1259.

2-Methoxy-9-(2-methyl-1-phenylprop-1-en-1-yl)phenanthrene (2p)



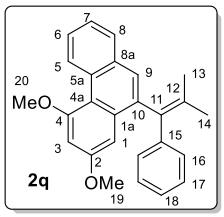
Obtained as yellow solid (131 mg, 0.39 mmol, 97%) from **1p** (135 mg). R_f = 0.25 (Hexane/EtOAc 40:1). M.p.: 142−144 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.66-8.57 (m, 2H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 6.9 Hz, 1H), 7.57 (s, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.41-7.34 (m, 2H), 7.31-7-23 (m, 4H), 7.17 (t, *J* = 7.1 Hz, 1H), 3.96 (s, 3H), 2.08 (s, 3H), 1.68 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.3 (C), 142.5 (C), 140.5 (C), 134.6 (C), 133.4 (C), 133.3 (C), 130.9 (C), 130.3 (C), 129.3 (2 x CH), 127.9 (2 x CH), 127.2 (CH), 126.9 (CH), 126.4 (CH), 126.2 (CH), 125.7 (CH), 124.2 (CH + C), 122.4 (CH), 116.9 (CH), 108.5 (CH), 55.5 (CH_3), 23.2 (CH_3), 22.2 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O$ 339.1731; Found 339.1740.

2,4-Dimethoxy-10-(2-methyl-1-phenylprop-1-en-1-yl)phenanthrene (2q)



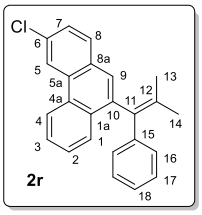
Obtained as white solid (109 mg, 0.30 mmol, 74%) from **1q** (147 mg). R_f = 0.22 (Hexane/EtOAc 9:1). M.p.: 108−110 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 9.56 (d, *J* = 8.5 Hz, 1H, H-5), 7.86 (d, *J* = 7.7 Hz, 1H, H-8), 7.65 (s, 1H, H-9), 7.62−7.51 (m, 2H, H-6, H-7), 7.37 (d, *J* = 7.1 Hz, 2H, H-16), 7.26 (t, *J* = 7.1 Hz, 2H, H-17), 7.22−7.13 (m, 2H, H-1,H-18), 6.79 (d, *J* = 2.5 Hz, 1H, H-3), 4.10 (s, 3H, H-20), 3.88 (s, 3H, H-19), 2.08 (s, 3H, H-13/14), 1.72 (s, 3H, H-13/14).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 160.4 (C, C-4), 158.2 (C, C-2), 142.3 (C, C-15), 139.0 (C, C-10), 135.5 (C, C-11), 134.9 (C, C-1a), 133.5 (C, C-12), 131.6 (C, C-8a), 130.0 (C, C-5a), 129.6 (CH, C-9), 129.44 (2 x CH, C-16), 128.35 (CH, C-8), 127.9 (2 x CH, C-17), 127.7 (CH, C-5), 126.3 (2 x CH, C-6, C-18), 125.1 (CH, C-7), 116.3 (C, C-4a), 100.3 (CH, C-1), 99.1 (CH, C-3), 55.9 (CH_3, C-20), 55.4 (CH_3, C-19), 23.2 (CH_3, C-13/14), 22.1 (CH_3, C-13/14).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{25}O_2$ 369.1849; Found 369.1852.

3-Chloro-9-(2-methyl-1-phenylprop-1-en-1-yl)phenanthrene (2r)



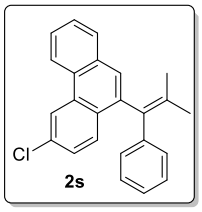
Obtained as colorless oil (136 mg, 0.39 mmol, 99%) from **1r** (137 mg). R_f = 0.33 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.64 (s, 1H, H-5), 8.61 (d, *J* = 7.5 Hz, 1H, H-4), 8.12 (d, *J* = 7.3 Hz, 1H, H-1), 7.77 (d, *J* = 8.5 Hz, 1H, H-8), 7.66−7.58 (m, 2H, H-2, H-3), 7.57 (s, 1H, H-9), 7.53 (d, *J* = 8.5 Hz, 1H, H-7), 7.34 (d, *J* = 7.1 Hz, 2H, H-16), 7.25 (t, *J* = 7.6 Hz, 2H, H-17), 7.16 (t, *J* = 7.2 Hz, 1H, H-18), 2.05 (s, 3H, H-13/14), 1.64 (s, 3H, H-13/14).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 142.3 (C, C-15), 140.3 (C, C-10), 134.3 (C, C-11), 133.9 (C, C-12), 132.3 (C, C-6), 131.7 (C, C-1a), 131.0 (C, C-5a), 130.3 (C, C-8a), 130.0 (CH, C-8), 129.9 (C, C-4a), 129.3 (2 x CH, C-16), 128.0 (2 x CH, C-17), 127.4 (CH, C-3), 127.2 (CH, C-7), 127.0 (CH, C-9), 126.9 (CH, C-1), 126.7 (CH, C-2), 126.4 (CH, C-18), 123.1 (CH, C-4), 122.3 (CH, C-5), 23.1 (CH_3, C-13/14), 22.1 (CH_3, C-13/14).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1258.

3-Chloro-10-(2-methyl-1-phenylprop-1-en-1-yl)phenanthrene (2s)



Obtained as white solid (130 mg, 0.38 mmol, 95%) from **1s** (137 mg). R_f = 0.23 (Hexane). M.p.: 172−174 ºC.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.65 (d, *J* = 2.1 Hz, 1H), 8.57 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 9.3 Hz, 1H), 7.68−7.58 (m, 3H), 7.50 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.34-7.29 (m, 2H), 7.26−7.21 (m, 2H), 7.19-7.12 (m, 1H), 2.05 (s, 3H), 1.64 (s, 3H).

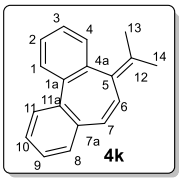
^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 142.2 (C), 139.4 (C), 134.2 (C), 134.0 (C), 132.6 (C), 132.4 (C), 132.1 (C), 129.8 (C), 129.3 (2 x CH), 128.9 (C), 128.7 (CH), 128.5 (CH), 128.04 (2 x CH), 127.95 (CH), 127.4 (CH), 127.3 (CH), 126.7 (CH), 126.4 (CH), 122.70 (2 x CH), 23.1 (CH_3), 22.1 (CH_3).

HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{19}ClNa$ 365.1067; Found 365.1072.

Cycloisomerization of terminal substrate 1k: Synthesis of phenanthrene 2k and dibenzocycloheptene 4k

Following the general procedure, a ~1:1 mixture of phenanthrene **2k** and dibenzocycloheptene **4k** was obtained from substrate **1k** (93 mg). The compounds were separated by flash chromatography on silica gel using hexane as eluent giving **2k** (41 mg, 0.18 mmol, 44%) and **4k** (51 mg, 0.22 mmol, 55%). Similar result was observed using TMS-substrate **1i.**

5-(propan-2-ylidene)-5H-dibenzo[a,c]cycloheptene (4k)



White solid. R_f = 0.32 (Hexane). M.p.: 65−67 ºC.

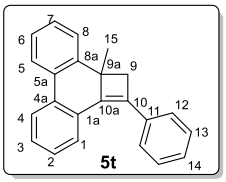
^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.70−7.66 (m, 1H, H-11), 7.56−7.53 (m, 1H, H-1), 7.38−7.31 (m, 4H, H-2, H-3, H-9, H-10), 7.30−7.27 (m, 1H, H-8), 7.17−7.14 (m, 1H, H-4), 6.67 (d, *J* = 11.0 Hz, 1H, H-6), 6.53 (d, *J* = 11.0 Hz, 1H, H-7), 1.80 (s, 3H, H-13/14), 1.71 (s, 3H, H-13/14).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 143.7 (C, C-4a), 139.8 (C, C-11a), 138.3 (C, C-1a), 136.4 (C, C-7a), 135.4 (CH, C-6), 131.5 (C, C-12), 131.2 (C, C-5), 130.5 (CH, C-1), 130.0 (CH, C-11), 129.3 (CH, C-8), 129.2 (CH, C-4), 128.0 (CH, C-7), 127.2 (CH, C-2/3/9/10), 126.9 (CH, C-2/3/9/10), 126.7 (CH, C-2/3/9/10), 126.6 (CH, C-2/3/9/10), 21.4 (CH_3, C-13/14), 20.7 (CH_3, C-13/14).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}$ 233.1325; Found 233.1325.

Cycloisomerization of α–disubstituted-β, β-unsubstituted styrene substrate 1t: Synthesis of dihydrocyclobutaphenanthrene 5t or phenanthrene 2t.

Synthesis of 10b-methyl-2-phenyl-1,10b-dihydrocyclobuta[*l*]phenanthrene 5t:



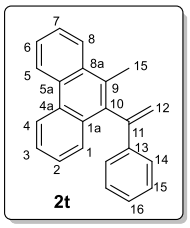
Obtained as yellow solid (94 mg, 0.32 mmol, 80%) from substrate **1t** (118 mg) by following the general procedure but stirring the reaction mixture for 24 h. R_f = 0.22 (Hexane). M.p.: 105−107 ºC.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.93 (dd, *J* = 5.6, 3.4 Hz, 1H, H-4), 7.82 (d, *J* = 7.3 Hz, 1H, H-5), 7.77 (dd, *J* = 5.6, 3.5 Hz, 1H, H-1), 7.61 (d, *J* = 7.2 Hz, 2H, H-12), 7.44−t7.40 (m, 2H, H-2, H-3), 7.39−7.33 (m, 3H, H-8, H-13), 7.33−7.24 (m, 3H, H-6, H-7, H-14), 3.28 (d, *J* = 12.7 Hz, 1H, H-9), 3.15 (d, *J* = 12.7 Hz, 1H, H-9), 1.44 (s, 3H, H-15).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 144.6 (C, C-8a), 143.1 (C, C-10a), 136.8 (C, C-10), 135.7 (C, C-11), 135.3 (C, C-4a), 133.8 (C, C-5a), 130.9 (C, C-1a), 128.5 (2 x CH, C-13), 128.4 (CH, C-3), 128.1 (CH, C-7), 127.9 (CH, C-2), 127.8 (CH, C-14), 126.6 (CH, C-6), 126.1 (CH, C-8), 126.0 (CH, C-1), 125.8 (2 x CH, C-12), 125.1 (CH, C-5), 124.4 (CH, C-4), 42.4 (CH_2, C-9), 41.9 (C, C-9a), 27.0 (CH_3, C-15).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}$ 295.1481; Found 295.1483.

Synthesis of 9-methyl-10-(1-phenylvinyl)phenanthrene 2t:



Obtained as colorless oil (85 mg, 0.29 mmol, 91%) by heating **5t** (94 mg, 0.32 mmol) for 24 h in DCE at 90 ºC. Alternatively, **2t** (113 mg, 0.38 mmol, 96%) could be directly obtained from substrate **1t** (118 mg) by following the general procedure but stirring the reaction mixture in DCE for 24 h at 90 ºC. R_f = 0.17 (Hexane).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.78 (d, *J* = 9.6 Hz, 1H, H-5), 8.72 (d, *J* = 8.3 Hz, 1H, H-4), 8.17 (d, *J* = 9.5 Hz, 1H, H-8), 7.91 (d, *J* = 8.1 Hz, 1H, H-1), 7.73−7.64 (m, 2H, H-6, H-7), 7.58 (t, *J* = 8.2 Hz, 1H, H-3), 7.46 (t, *J* = 8.2 Hz, 1H, H-2), 7.41−7.36 (m, 2H, H-14), 7.27−7.24 (m, 3H, H-15, H-16), 6.28 (d, *J* = 1.2 Hz, 1H, H-12), 5.31 (d, *J* = 1.2 Hz, 1H, H-12), 2.64 (s, 3H, H-15).

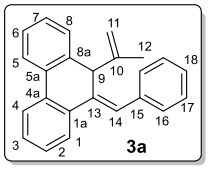
^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 146.8 (C, C-11), 139.9 (C, C-13), 136.4 (C, C-10), 132.1 (C, C-9), 131.8 (C, C-8a), 130.1 (C, C-1a/C-5a), 130.0 (C, C-1a/C-5a), 129.7 (C, C-4a), 128.7 (2 x CH, C-15), 127.9 (CH, C-16), 127.4 (CH, C-1), 126.9 (CH, C-2/6/7), 126.8 (CH, C-2/6/7), 126.4 (CH, C-2/6/7), 126.3 (2 x CH, C-14), 125.9 (CH, C-3), 125.2 (CH, C-8), 123.0 (CH, C-5), 122.5 (CH, C-4), 116.4 (CH_2, C-12), 17.2 (CH_3, C-15).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}$ 295.1481; Found 295.1484.

General procedure for the synthesis of dihydrophenanthrenes 3.

In a round bottom flask, PPh_3AuNTf_2 (5 mol%, 31 mg) was added to a solution of the corresponding 2-alkenyl-2'-alkynyl-1,1'-biphenyl **1** (1 equiv., 0.4 mmol) in THF (8 mL, 0.05 M) and the reaction mixture was stirred for 72 h at RT or 50 ºC. The resulting mixture was filtered over a plug of Celite eluting with a mixture of hexane/EtOAc 40:1 and solvents were removed under reduced pressure. The crude reaction was purified by flash chromatography on silica gel using mixtures of hexane and EtOAc as eluents to give the corresponding dihydrophenanthrenes **3**.

(*E*)-9-Benzylidene-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3a)



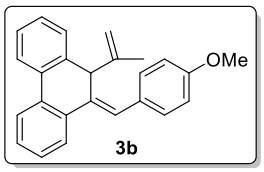
Obtained as colorless oil (97 mg, 0.31 mmol, 79%) from **1a** (123 mg). R_f = 0.22 (Hexane).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.83 (d, *J* = 8.0 Hz, 1H, H-4), 7.81 (d, *J* = 7.9 Hz, 1H, H-5), 7.64 (d, *J* = 7.4 Hz, 1H, H-1), 7.45–7.40 (m, 4H, H-16, H-17), 7.40–7.30 (m, 4H, H-2, H-3, H-6, H-18), 7.25–7.18 (m, 2H, H-7, H-8), 7.05 (s, 1H, H-14), 4.74 (m, 1H, H-11), 4.70 (s, 1H, H-11), 4.67 (s, 1H, H-9), 1.63 (s, 3H, H-12).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.4 (C, C-10), 139.1 (C, C-13), 137.31 (C, C-15), 137.30 (C-8a), 137.1 (C-1a), 133.21 (C, C-5a), 133.16 (C, C-4a), 129.6 (CH, C-8), 129.2 (2 x CH, C-16), 128.9 (CH, C-14), 128.5 (CH, C-2), 128.41 (2 x CH, C-17), 128.36 (CH, C-3), 127.49 (CH, C-6/7), 127.46 (CH, C-6/C-7), 127.2 (CH, C-18), 126.1 (CH, C-1), 124.0 (CH, C-5), 123.2 (CH, C-4), 112.7 (CH_2, C-11), 49.0 (CH, C-9), 21.6 (CH_3, C-12).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}$ 309.1638; Found 309.1637.

(*E*)-9-(4-Methoxybenzylidene)-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3b)



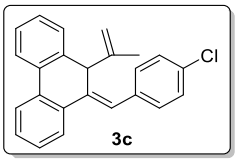
Following the general procedure using compound **1b** (135 mg) a no separable 1.2:1 mixture (80 mg, 0.24 mmol, 59%) of dihydrophenathrene **3b** and phenanthrene **2b** was obtained. R_f = 0.25 (Hexane/EtOAc 40:1). The data of **3b** are obtained from the mixture.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.87–7.75 (m, 1H), 7.65–7.50 (m, 3H), 7.36–7.32 (m, 3H), 7.26–7.22 (m, 1H), 7.20–7.18 (m, 2H), 6.97 (s, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.71 (bs, 2H), 4.64 (s, 1H), 3.86 (s, 3H), 1.63 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 158.7 (C), 146.4 (C), 137.5 (C), 137.3 (2 x C), 133.1 (C), 132.9 (C), 130.40 (2 x CH), 129.8 (C), 129.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.3 (2 x CH), 126.0 (CH), 123.9 (CH), 123.1 (CH), 113.8 (CH), 112.5 (CH_2), 108.3 (CH), 55.5 (CH_3), 49.1 (CH), 21.7 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339.1741.

(*E*)-9-(4-Chlorobenzylidene)-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3c)



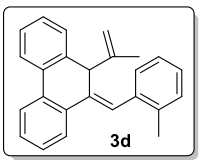
Obtained as yellow oil (130 mg, 0.38 mmol, 95%) from **1c** (137 mg). R_f = 0.19 (Hexane/EtOAc 40:1).

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.85–7.80 (m, 2H), 7.62 (d, *J* = 7.4 Hz, 1H), 7.45–7.29 (m, 7H), 7.27–7.15 (m, 2H), 6.97 (s, 1H), 4.74 (s, 1H), 4.71 (s, 1H), 4.57 (s, 1H), 1.61 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 146.2 (C), 140.0 (C), 137.0 (C), 136.8 (C), 135.7 (C), 133.2 (C), 133.1 (C), 133.0 (C), 130.5 (2 x CH), 129.5 (CH), 128.7 (CH), 128.6 (2 x CH), 128.4 (CH), 127.59 (CH), 127.57 (CH), 127.50 (CH), 126.1 (CH), 124.0 (CH), 123.3 (CH), 112.8 (CH_2), 49.1 (CH), 21.5 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1249.

(*E*)-9-(2-methylbenzylidene)-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3d)



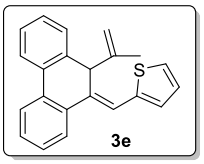
Obtained as colorless oil (90 mg, 0.28 mmol, 70%) from **1c** (129 mg). R_f = 0.14 (Hexane)

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 7.86-7.79 (m, 2H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.44–7.32 (m, 4H), 7.31–7.19 (m, 4H), 7.20–7.14 (m, 1H), 6.99 (s, 1H), 4.67–4.64 (m, 1H), 4.51 (s, 1H), 4.48 (s, 1H), 2.29 (s, 3H), 1.55 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 146.5 (C), 139.0 (C), 137.7 (C), 137.3 (C), 136.9 (C), 136.4 (C), 133.5 (C), 133.4 (C), 130.1 (CH), 129.4 (CH), 129.2 (CH), 128.4 (CH), 128.3 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 125.9 (CH), 125.6 (CH), 124.0 (CH), 123.2 (CH), 112.4 (CH_2), 48.9 (CH), 21.5 (CH_3), 20.3 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}$ 323.1794; Found 323.1795.

(*E*)-9-(2-Thienylmethylidene)-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3e)



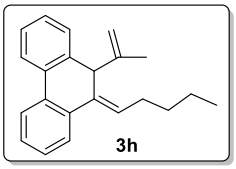
Following the general procedure, but under heating at 50 ºC, using compound **1e** (126 mg) a no separable 1:1.5 mixture (94 mg, 0.30 mmol, 75%) of dihydrophenathrene **3e** and phenanthrene **2e** was obtained. R_f = 0.20 (Hexane). The data of **3e** are obtained from the mixture.

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.81 (t, *J* = 6.3 Hz, 2H), 7.68–7.58 (m, 1H), 7.41–7.29 (m, 5H), 7.28–7.23 (m, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 7.11 (s, 1H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.05 (s, 1H), 4.71 (s, 1H), 4.62 (s, 1H), 1.70 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 145.6 (C), 140.0 (C), 137.5 (C), 137.1 (C), 136.7 (C), 133.3 (C), 133.2 (C), 129.7 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 127.63 (CH), 127.56 (CH), 127.3 (CH), 125.84 (CH), 125.79 (CH), 124.0 (CH), 123.3 (CH), 121.4 (CH), 112.7 (CH_2), 49.5 (CH), 21.5 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}S$ 315.1202; Found 315.1199.

(*E*)-9-Butylidene-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3h)



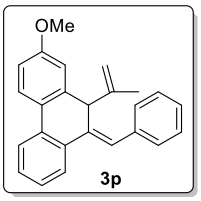
Obtained as colorless oil (79 mg, 0.27 mmol, 69%) from **1h** (115 mg) following the general procedure but heating at 50 ºC. R_f = 0.24 (Hexane)

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 8.08 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 2H), 7.57–7.52 (m, 3H), 6.24 (t, *J* = 7.3 Hz, 1H), 4.90 (s, 1H), 4.79 (s, 1H), 4.67 (s, 1H), 2.77–2.66 (m, 1H), 2.66–2.56 (m, 1H), 1.87 (s, 3H), 1.81–1.73 (m, 2H), 1.73–1.65 (m, 2H), 1.22 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.7 (C), 138.1 (C), 136.5 (C), 136.0 (C), 133.9 (C), 132.9 (C), 129.9 (CH), 129.4 (CH), 128.1 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 125.6 (CH), 123.8 (CH), 123.1 (CH), 111.9 (CH_2), 48.5 (CH), 32.0 (CH_2), 28.0 (CH_2), 22.7 (CH_2), 21.1 (CH_3), 14.2 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}$ 275.1794; Found 275.1793.

(*E*)-9-Benzylidene-2-methoxy-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3p)



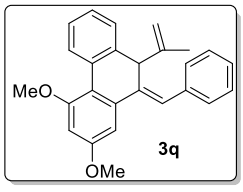
Obtained as colorless oil (129 mg, 0.38 mmol, 95%) from **1p** (135 mg) following the general procedure but heating at 50 ºC. R_f = 0.24 (Hexane).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.73 (dd, *J* = 7.7, 4.1 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 4.4 Hz, 3H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.33–7.31 (m, 1H), 7.28 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.03 (s, 1H), 6.86 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.74 (d, *J* = 2.8 Hz, 1H), 4.76-4.73 (m, 1H), 4.73 (s, 1H), 4.71 (s, 1H), 3.81 (s, 3H), 1.63 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 159.1 (C), 146.3 (C), 139.3 (C), 138.9 (C), 137.4 (C), 136.3 (C), 133.2 (C), 129.2 (2 x CH), 128.8 (CH), 128.5 (CH), 128.4 (2 x CH), 127.5 (CH), 127.1 (CH), 126.3 (C), 126.0 (CH), 125.3 (CH), 122.6 (CH), 114.7 (CH), 113.1 (CH), 112.7 (CH_2), 55.5 (CH_3), 49.3 (CH), 21.6 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O$ 339.1743; Found 339,1747.

(*E*)-10-Benzylidene-2,4-dimethoxy-9-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3q): Obtained as orange oil (108 mg, 0.29 mmol, 73%) from **1q** (147 mg). R_f = 0.18 (Hexane/EtOAc 9:1).



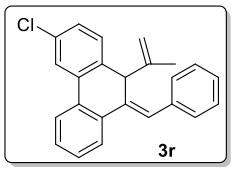
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.35 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 4.4 Hz, 4H), 7.35–7.22 (m, 2H), 7.17-7.09 (m, 2H), 7.04 (s, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.57 (d, *J* = 2.4 Hz, 1H), 4.78–4.75 (m, 1H), 4.67 (s, 1H), 4.59 (s, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 1.68 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ (ppm) 159.9 (C), 158.2 (C), 145.5 (C), 140.74 (C), 140.69 (C), 137.2 (C), 136.9 (C), 132.1 (C), 129.1 (2 x CH), 129.0 (CH), 128.42 (2 x

CH), 128.37 (CH), 127.9 (CH), 127.2 (CH), 126.7 (CH), 126.0 (CH), 115.8 (C), 112.5 (CH_2), 103.3 (CH), 99.3 (CH), 55.7 (CH_3), 55.5 (CH_3), 49.3 (CH), 21.9 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd $C_{26}H_{25}O_2$ 369.1849; Found 369.1844.

(*E*)-9-Benzylidene-3-chloro-10-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3r)



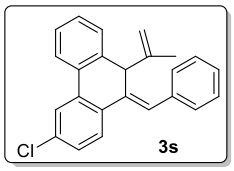
Obtained as colorless oil (114 mg, 83%) from **1r** (137 mg) following the general procedure but heating at 50 ºC. R_f = 0.19 (Hexane).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.79–7.74 (m, 2H), 7.66–7.61 (m, 1H), 7.43–7.34 (m, 6H), 7.34–7.28 (m, 1H), 7.18 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.04 (s, 1H), 4.74-4.72 (m, 1H), 4.66 (s, 1H), 4.62 (s, 1H), 1.59 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 145.9 (C), 138.4 (C), 137.12 (C), 137.10 (C), 135.7 (C), 135.0 (C), 133.3 (C), 132.0 (C), 130.8 (CH), 129.4 (CH), 129.2 (2 x CH), 129.0 (CH), 128.6 (CH), 128.5 (2 x CH), 127.34 (CH), 127.28 (CH), 126.21 (CH), 124.1 (CH), 123.3 (CH), 113.0 (CH_2), 48.4 (CH), 21.5 (CH_3).

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1244.

(*E*)-10-Benzylidene-3-chloro-9-(prop-1-en-2-yl)-9,10-dihydrophenanthrene (3s)



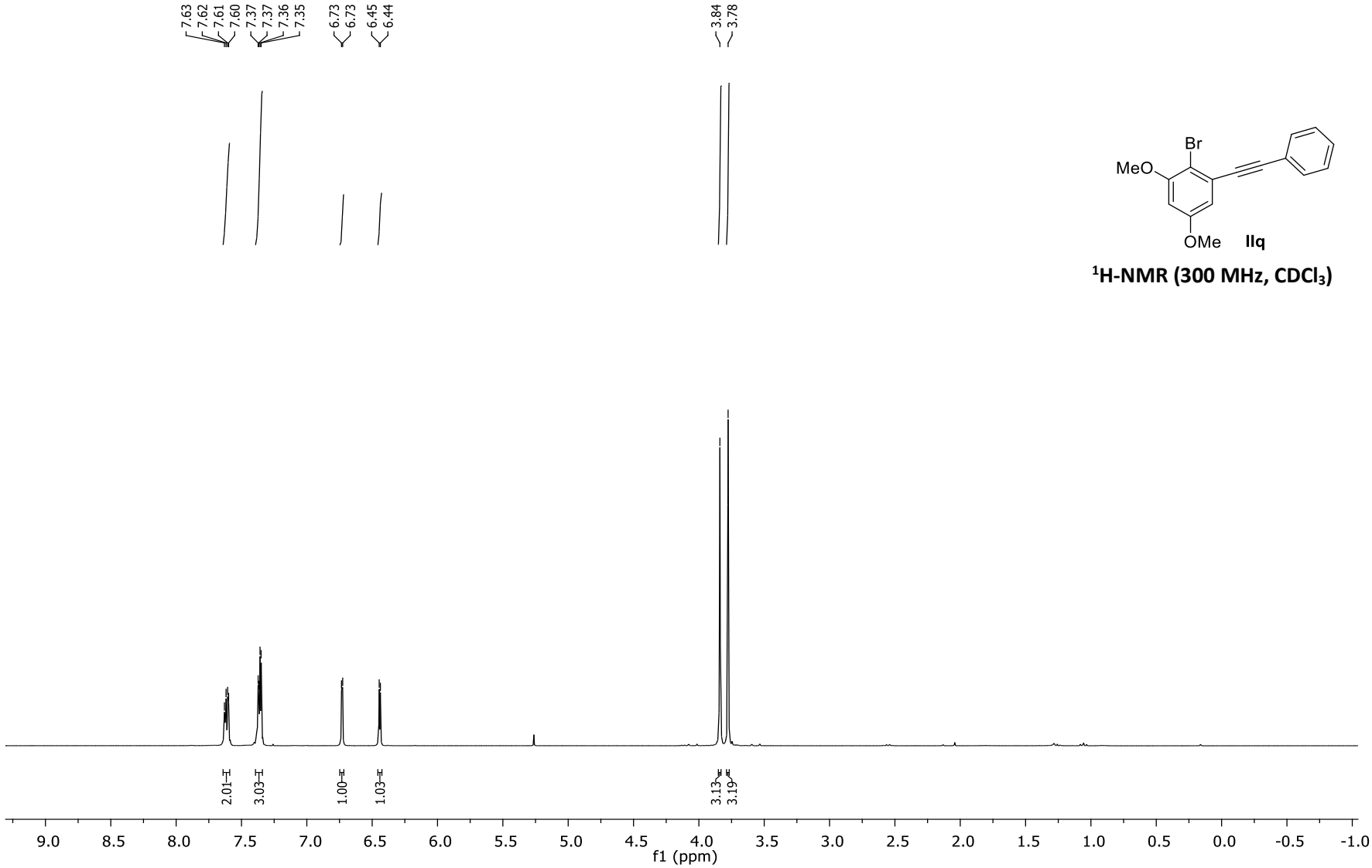
Obtained as colorless oil (114 mg, 0.33 mmol, 99%) from **1r** (137 mg) following the general procedure but heating at 50 ºC. R_f = 0.26 (Hexane).

^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 2.1 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 4.4 Hz, 4H), 7.37–7.27 (m, 3H), 7.27–7.22 (m, 1H), 7.22–7.18 (m, 1H), 7.01 (s, 1H), 4.75-4.74 (m, 1H), 4.66 (bs, 2H), 1.61 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ (ppm) 146.1 (C), 138.0 (C), 137.5 (C), 137.0 (C), 135.5 (C), 134.8 (C), 134.3 (C), 132.1 (C), 129.7 (CH), 129.3 (CH), 129.2 (2 x CH), 128.5 (2 x CH), 128.24 (CH), 128.15 (CH), 127.6 (CH), 127.42 (CH), 127.37 (CH), 124.1 (CH), 123.4 (CH), 112.9 (CH_2), 48.9 (CH), 21.6 (CH_3).

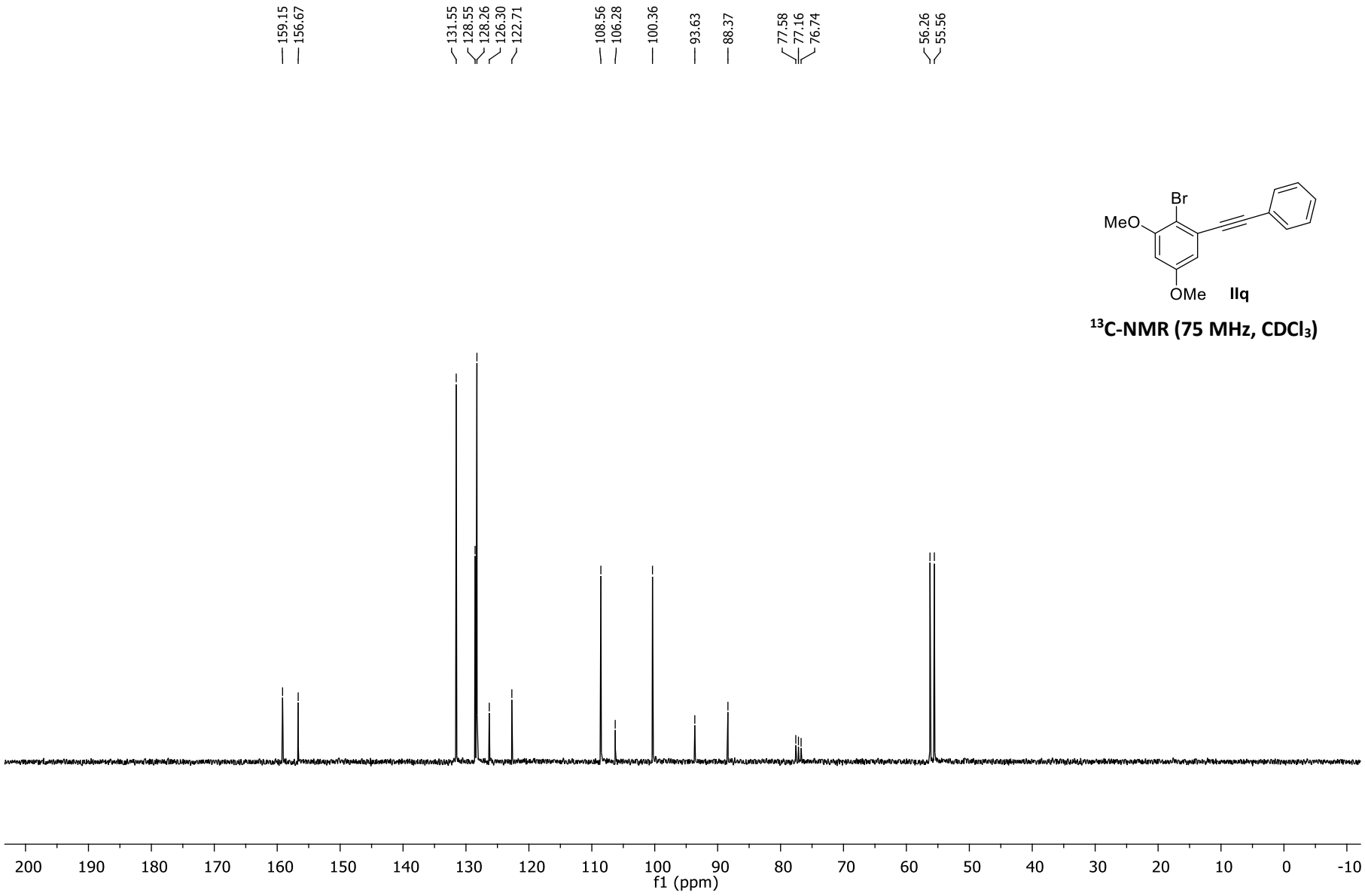
HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}Cl$ 343.1248; Found 343.1255.

Copies of ^{1}H and ^{13}C spectra for novel compounds and selected GCOSY, TOCSY, NOESY, GHSQC and GHMBC spectra



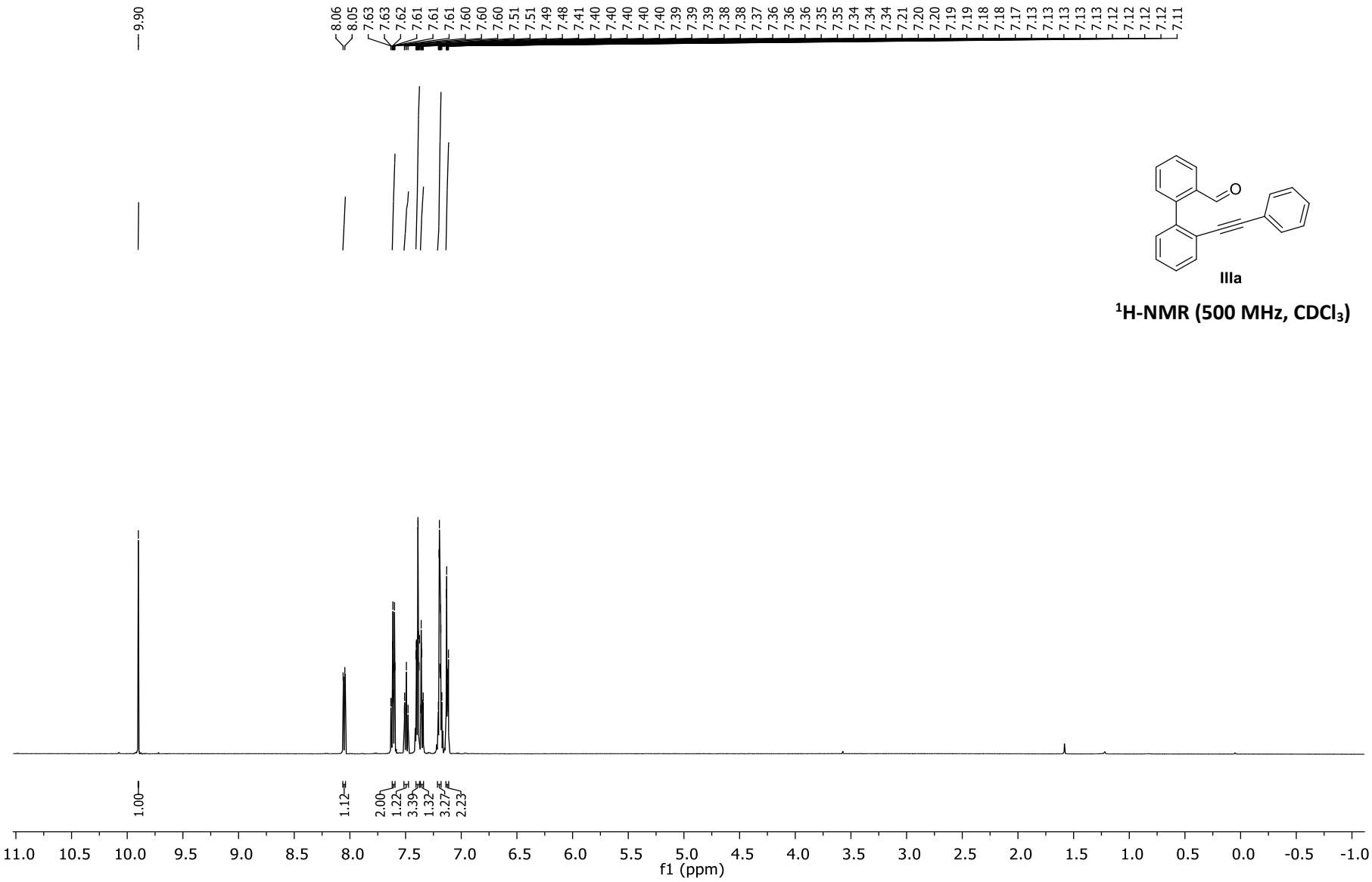
IIq

^{1}H-NMR (300 MHz, $CDCl_3$)



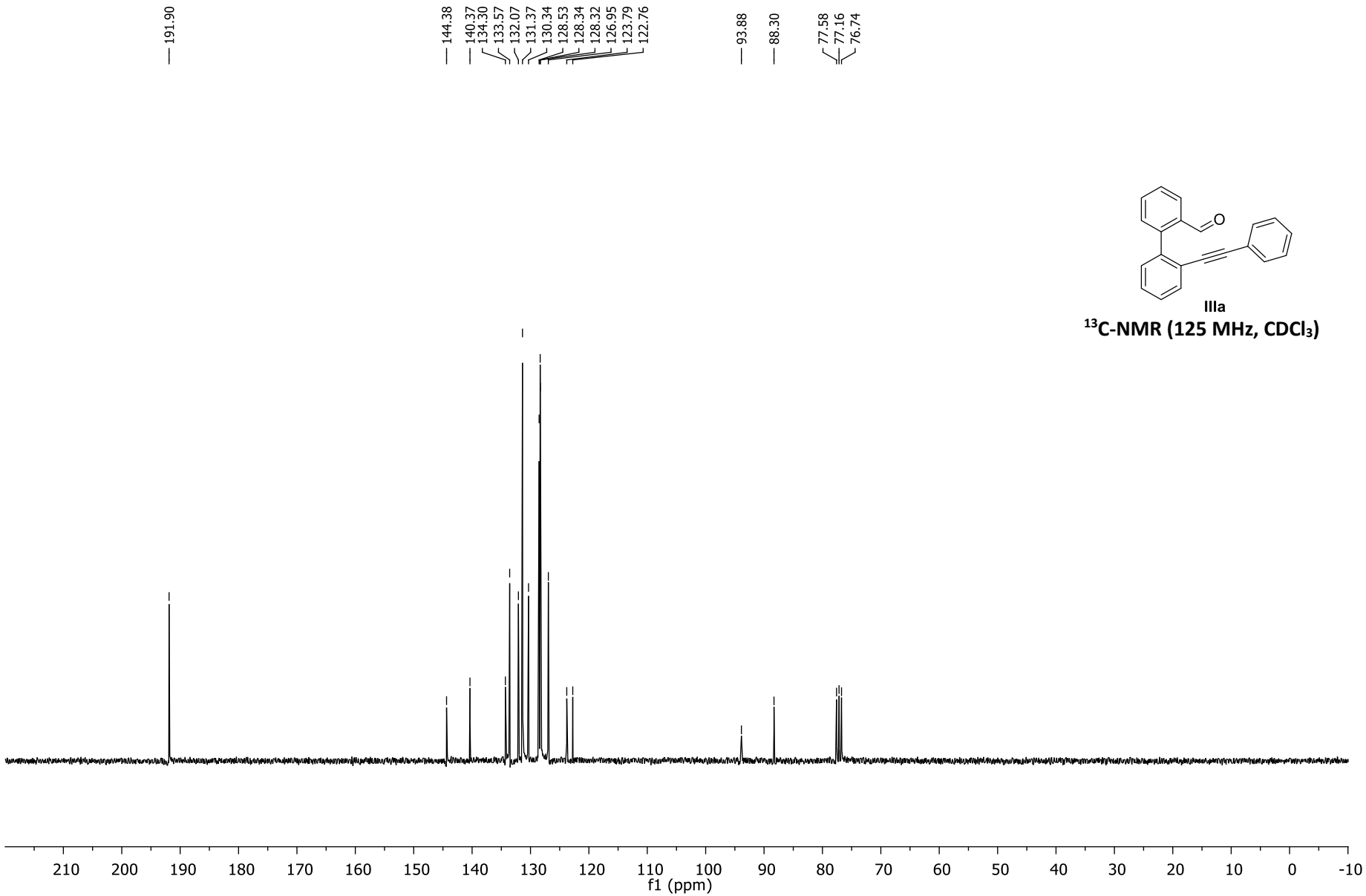
IIq

^{13}C-NMR (75 MHz, $CDCl_3$)



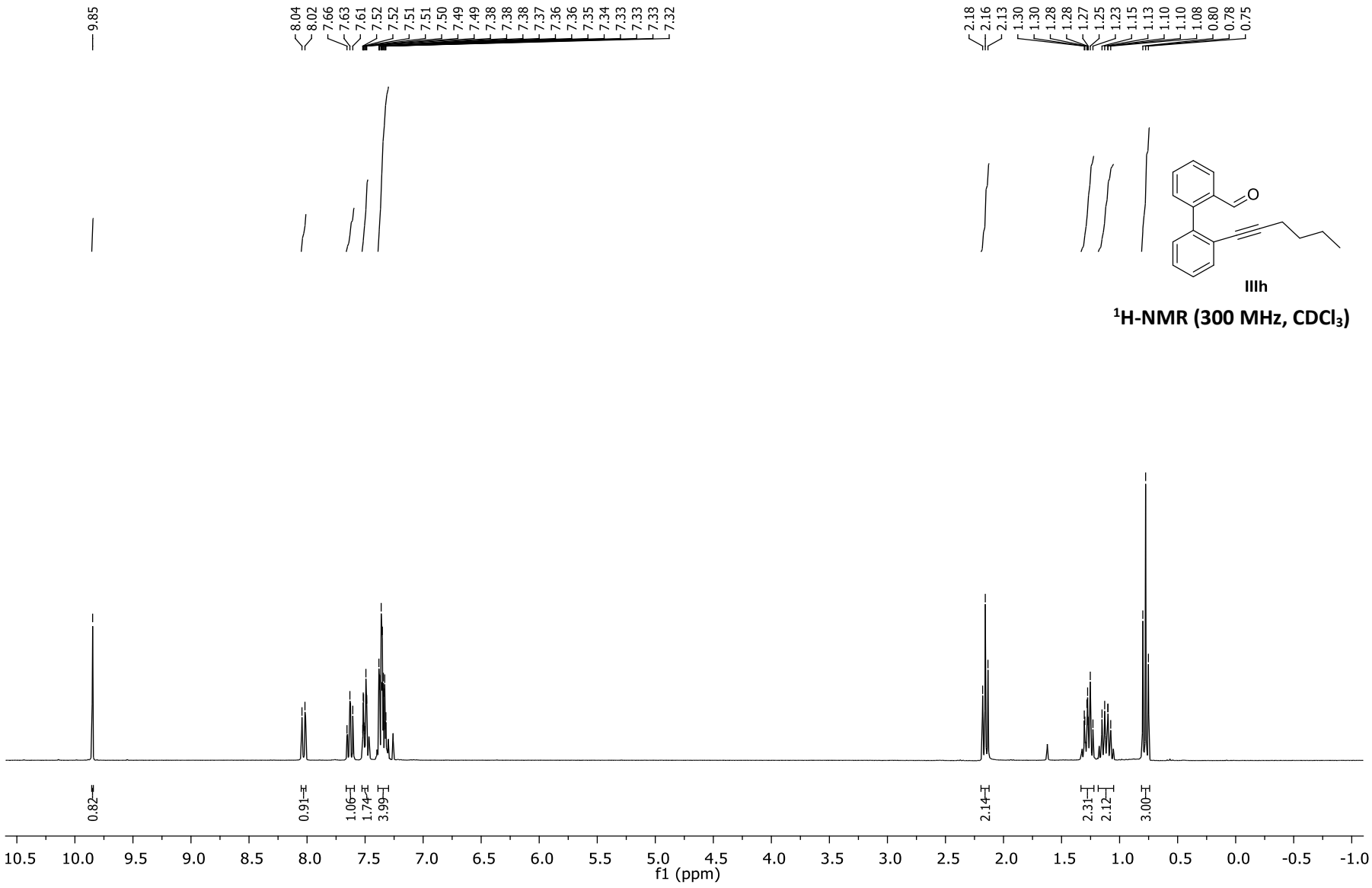
IIIa

^{1}H-NMR (500 MHz, $CDCl_3$)



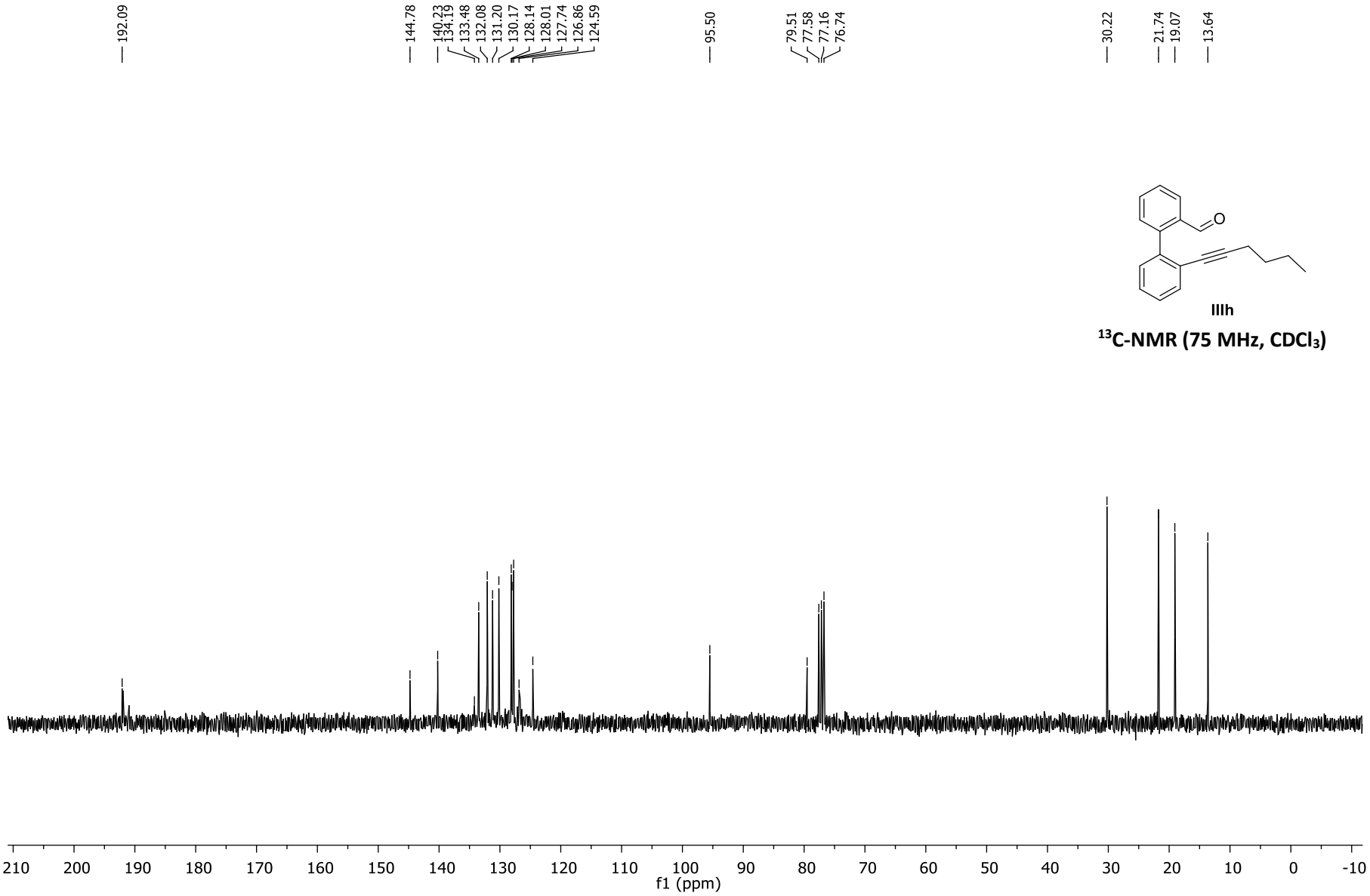
IIIa

^{13}C-NMR (125 MHz, $CDCl_3$)



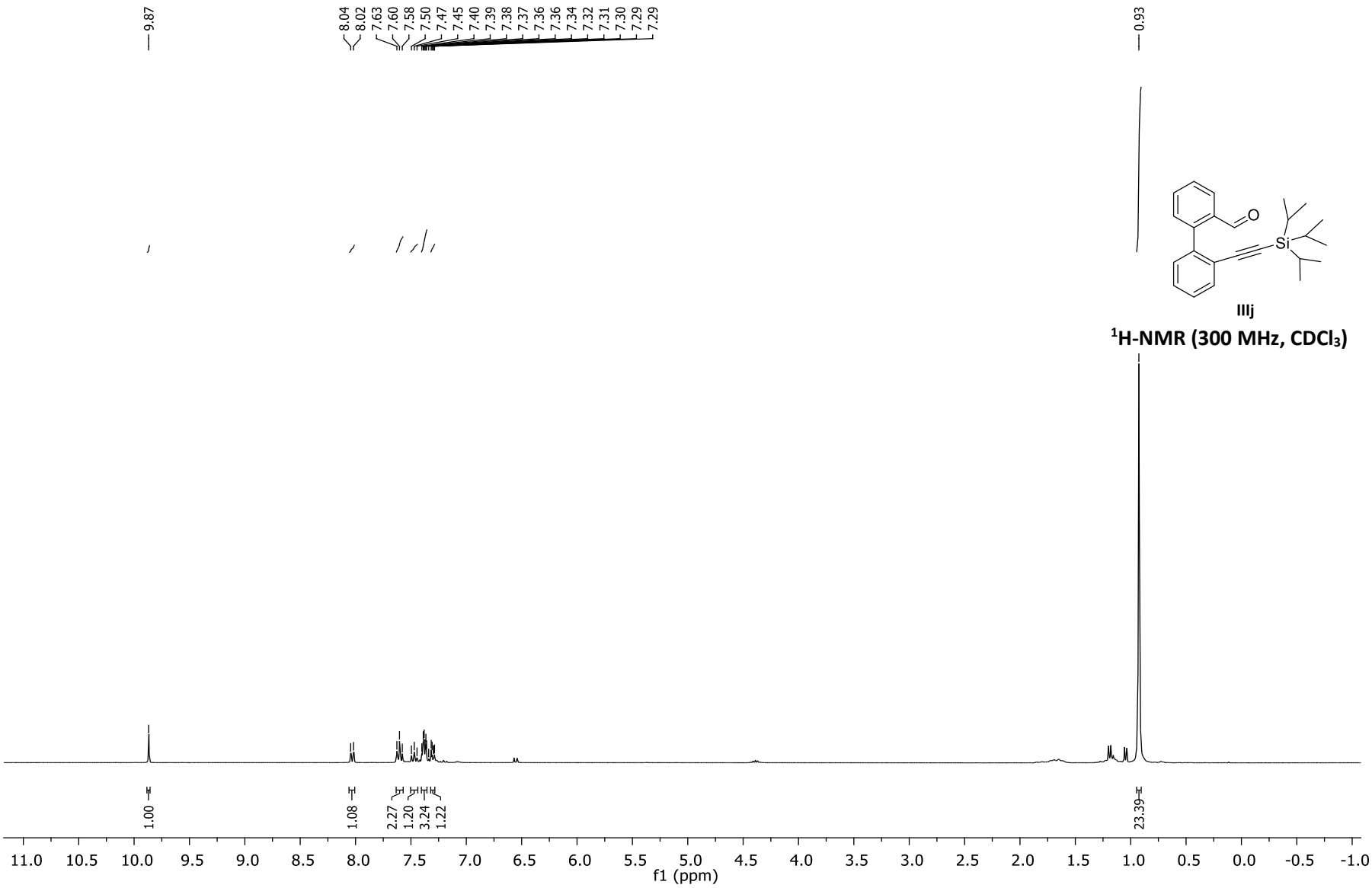
IIIh

^{1}H-NMR (300 MHz, $CDCl_3$)



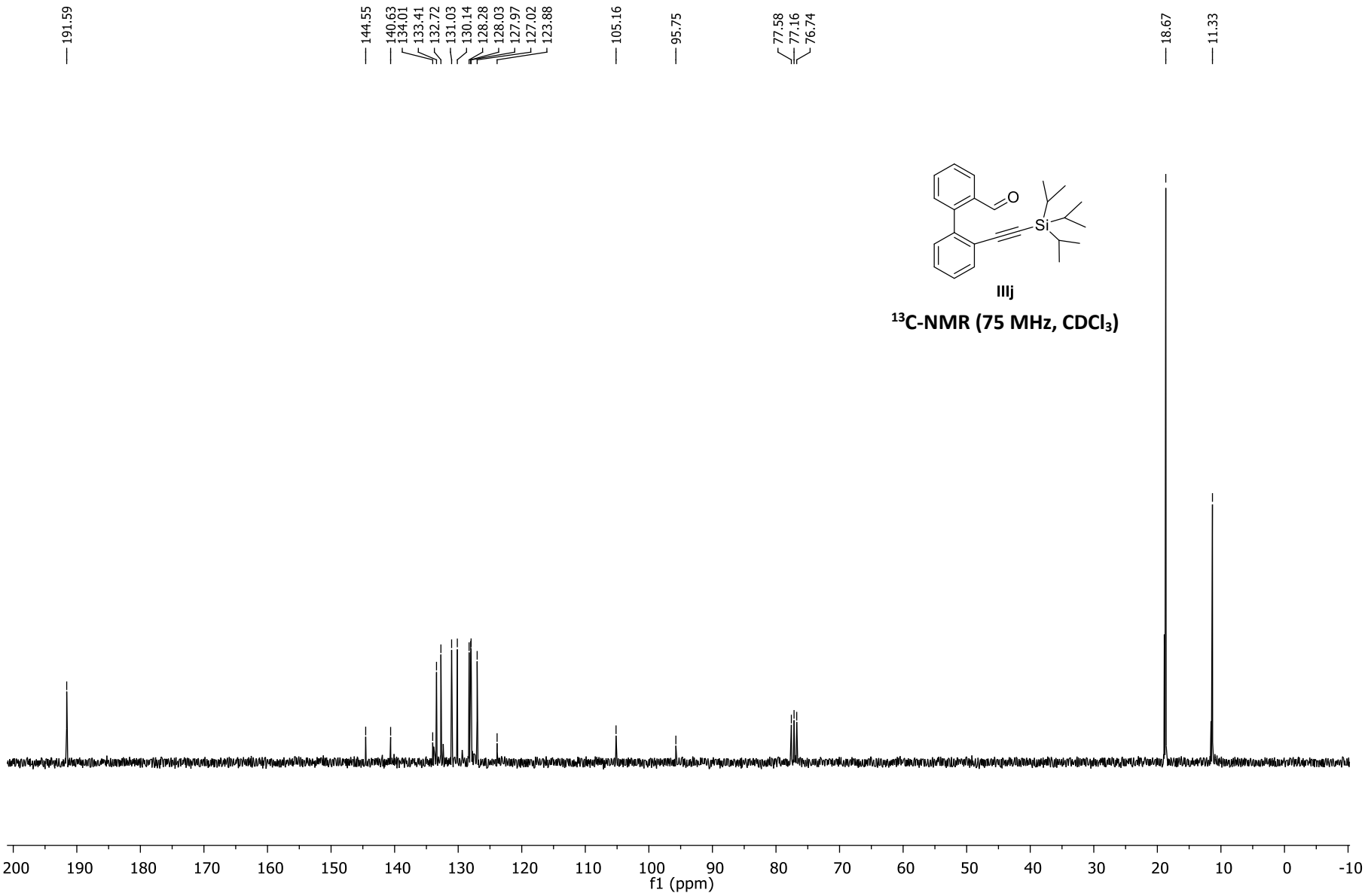
IIIh

^{13}C-NMR (75 MHz, $CDCl_3$)



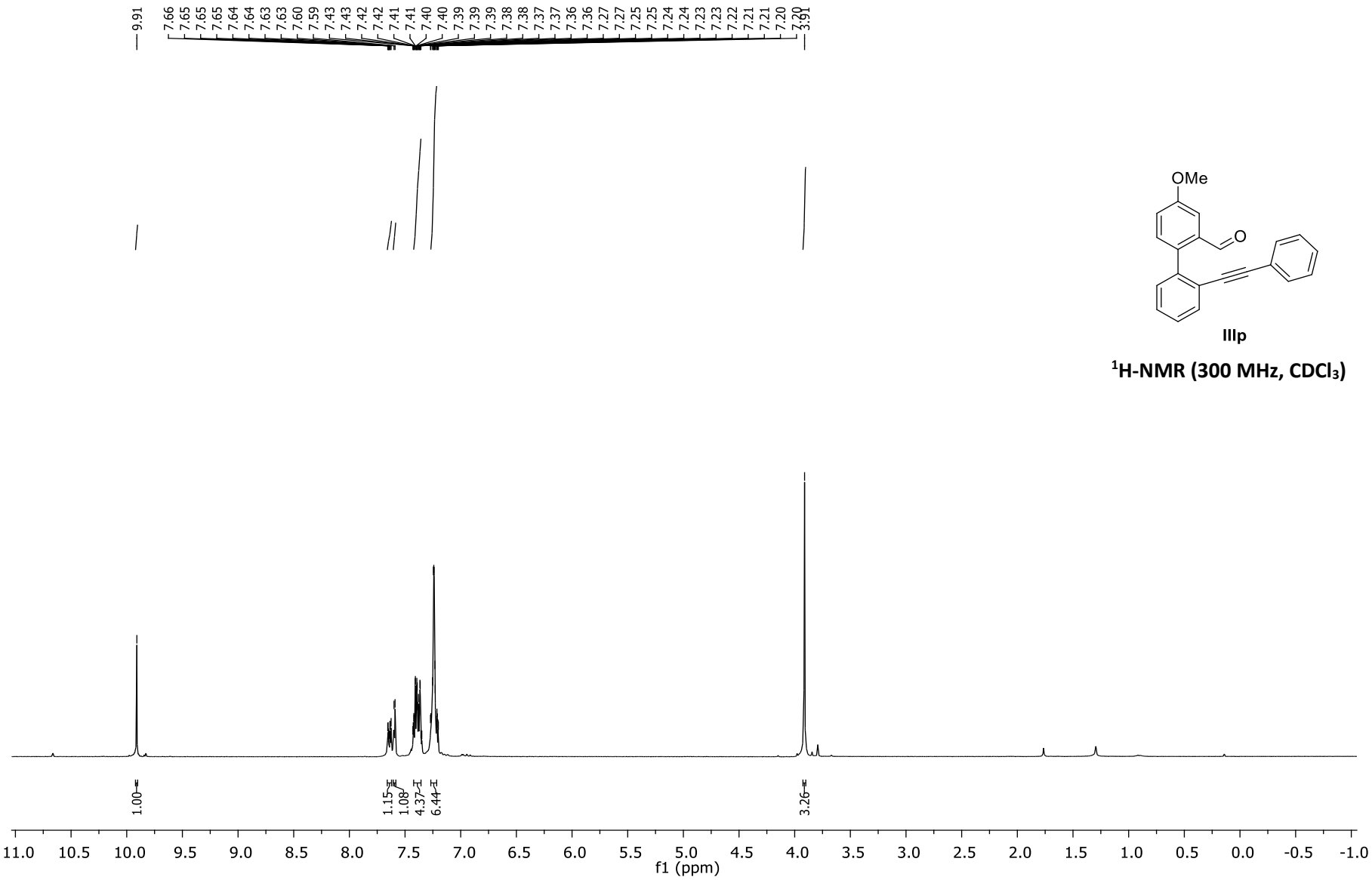
IIIj

^{1}H-NMR (300 MHz, $CDCl_3$)



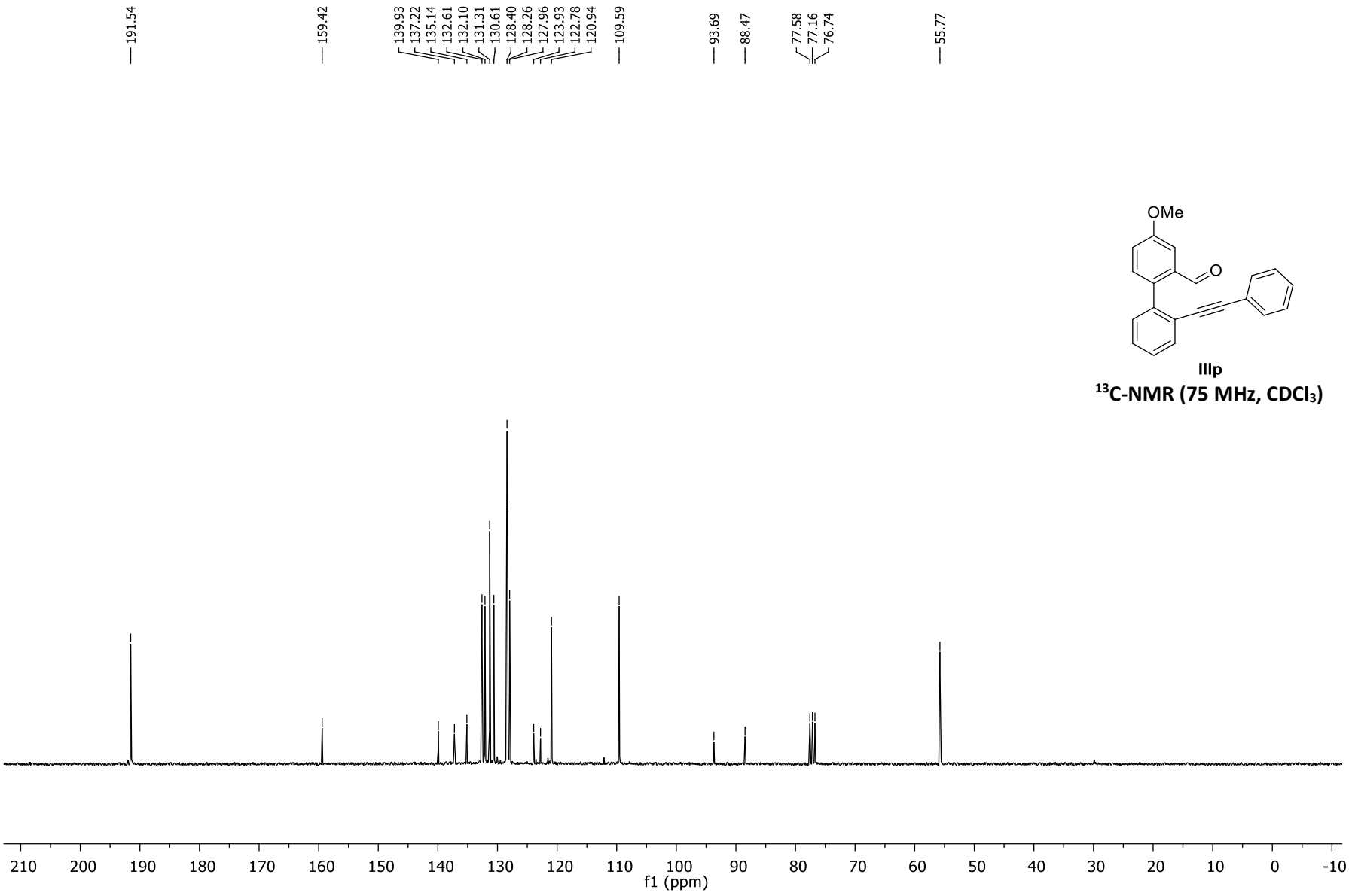
IIIj

^{13}C-NMR (75 MHz, $CDCl_3$)



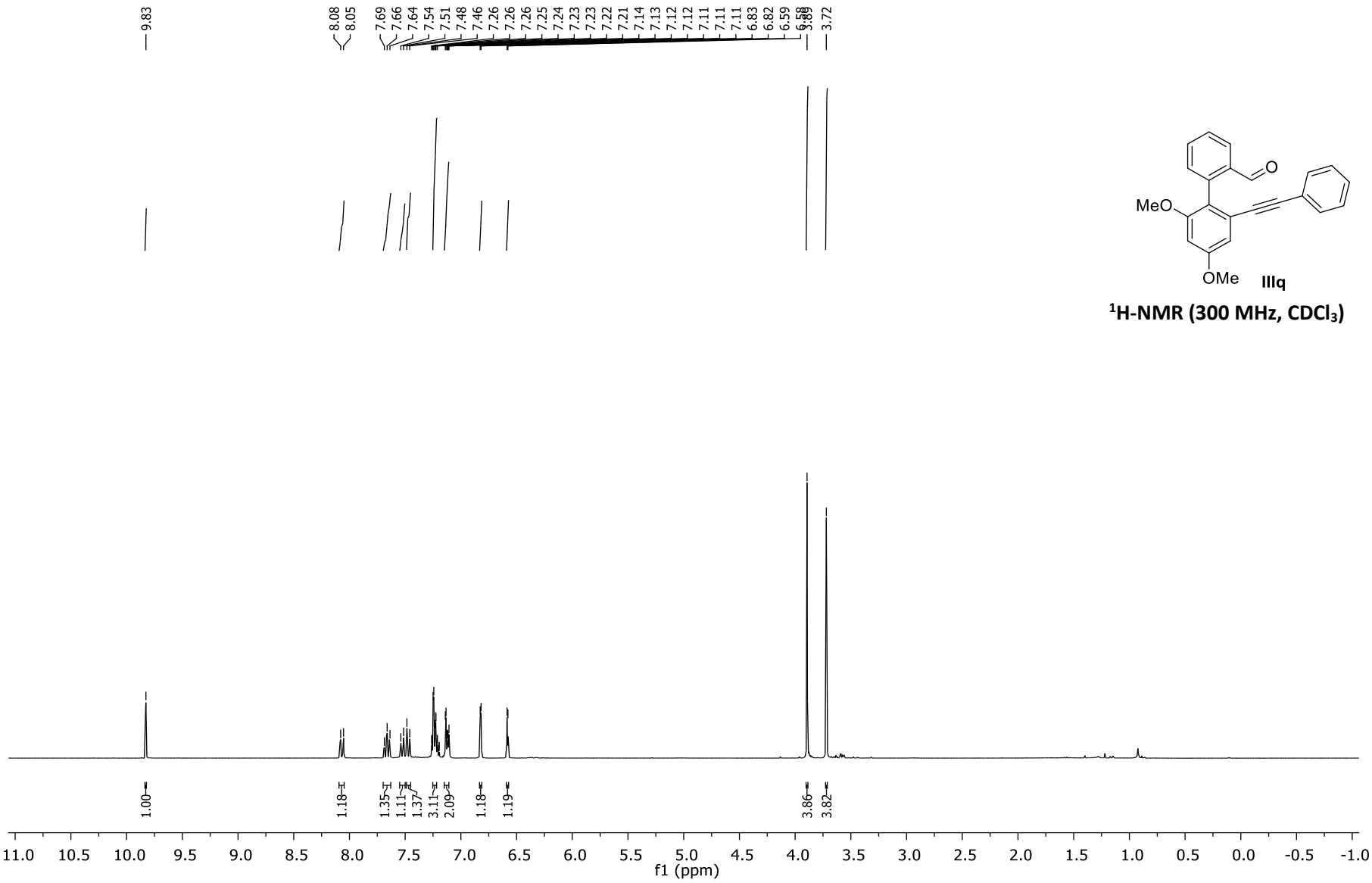
IIIp

^{1}H-NMR (300 MHz, $CDCl_3$)



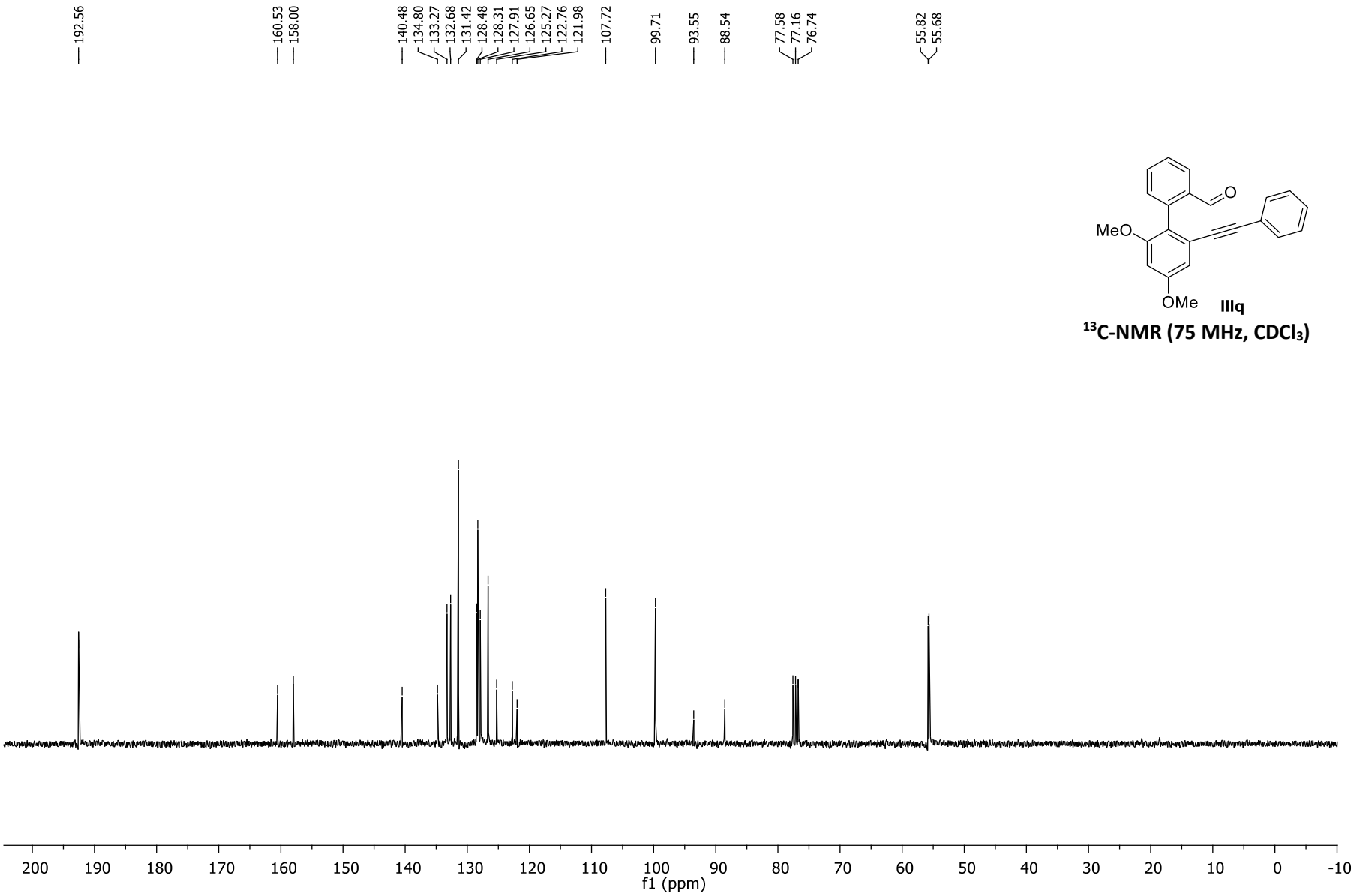
IIIp

^{13}C-NMR (75 MHz, $CDCl_3$)



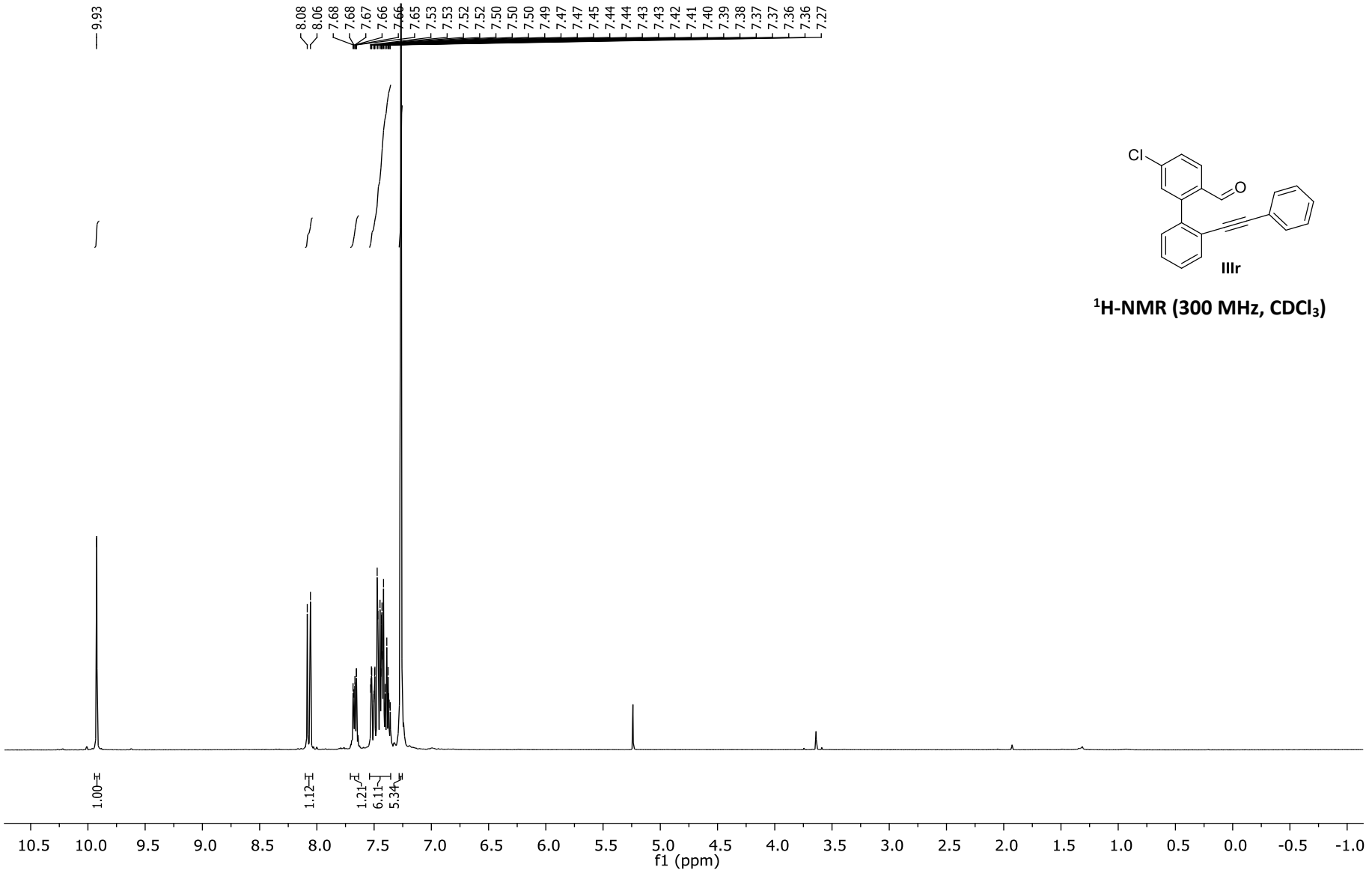
IIIq

^{1}H-NMR (300 MHz, $CDCl_3$)



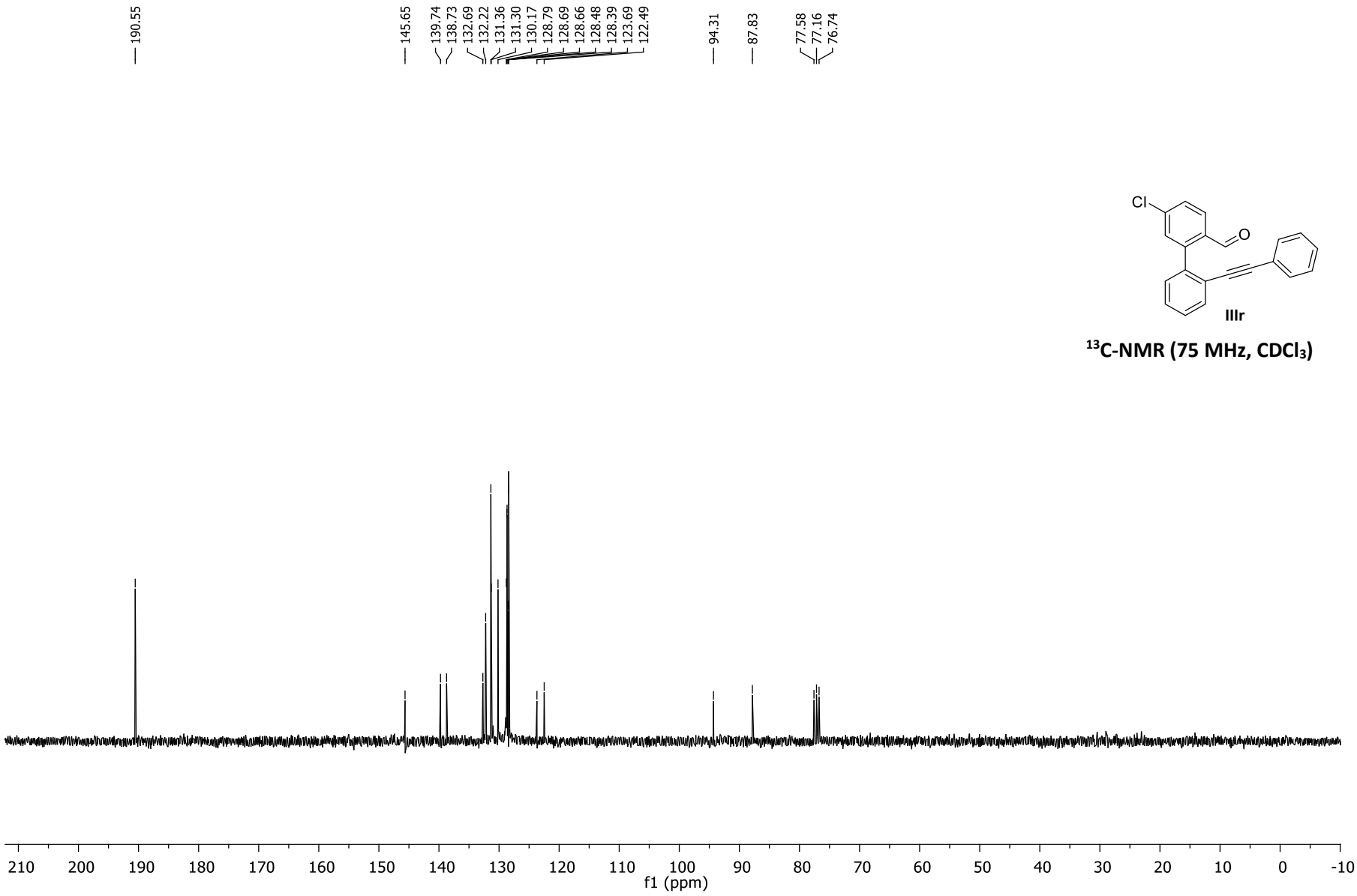
IIIq

^{13}C-NMR (75 MHz, $CDCl_3$)

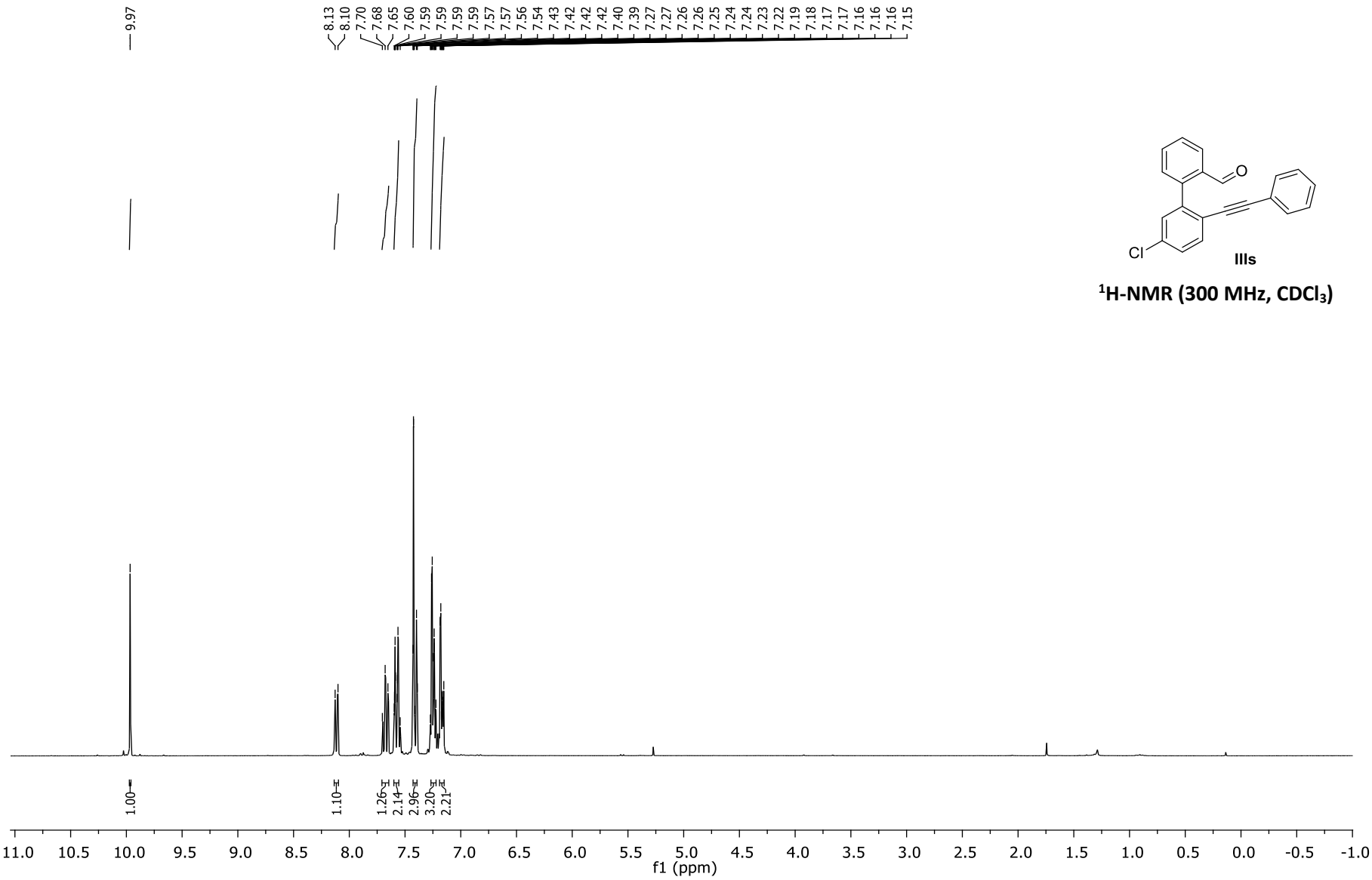


IIIr

^{1}H-NMR (300 MHz, $CDCl_3$)

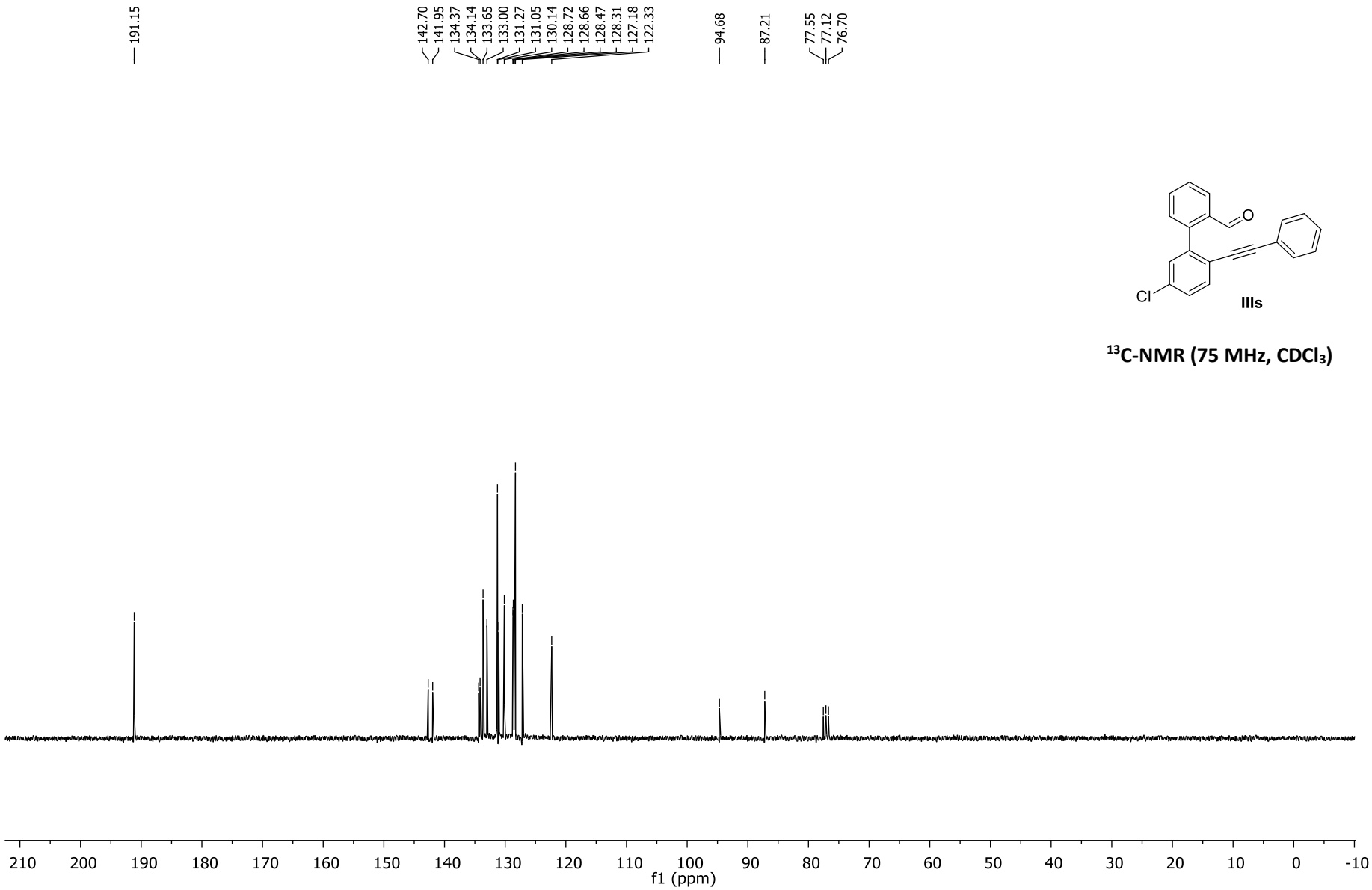


^{13}C-NMR (75 MHz, $CDCl_3$)

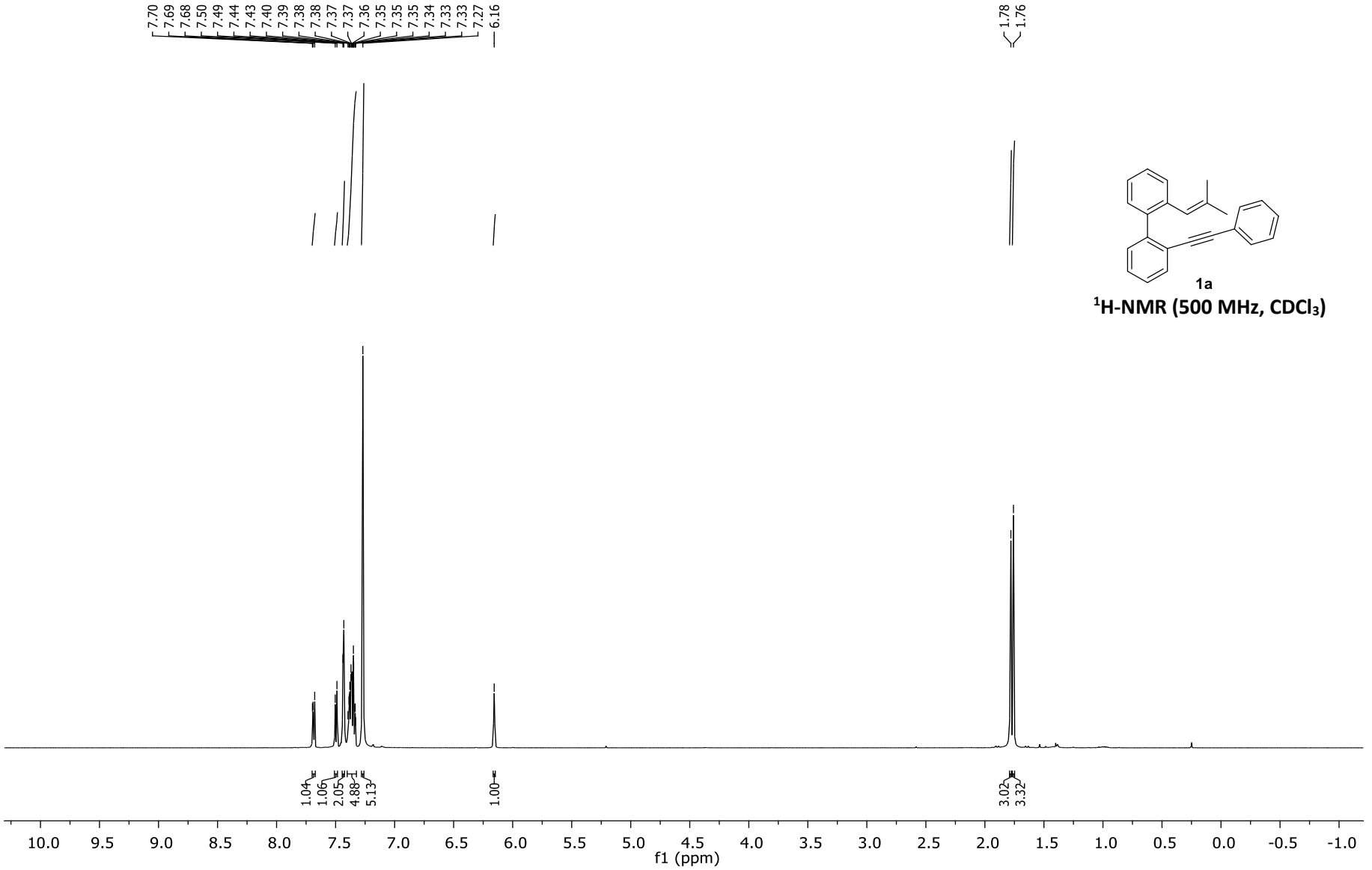


IIIs

^{1}H-NMR (300 MHz, $CDCl_3$)

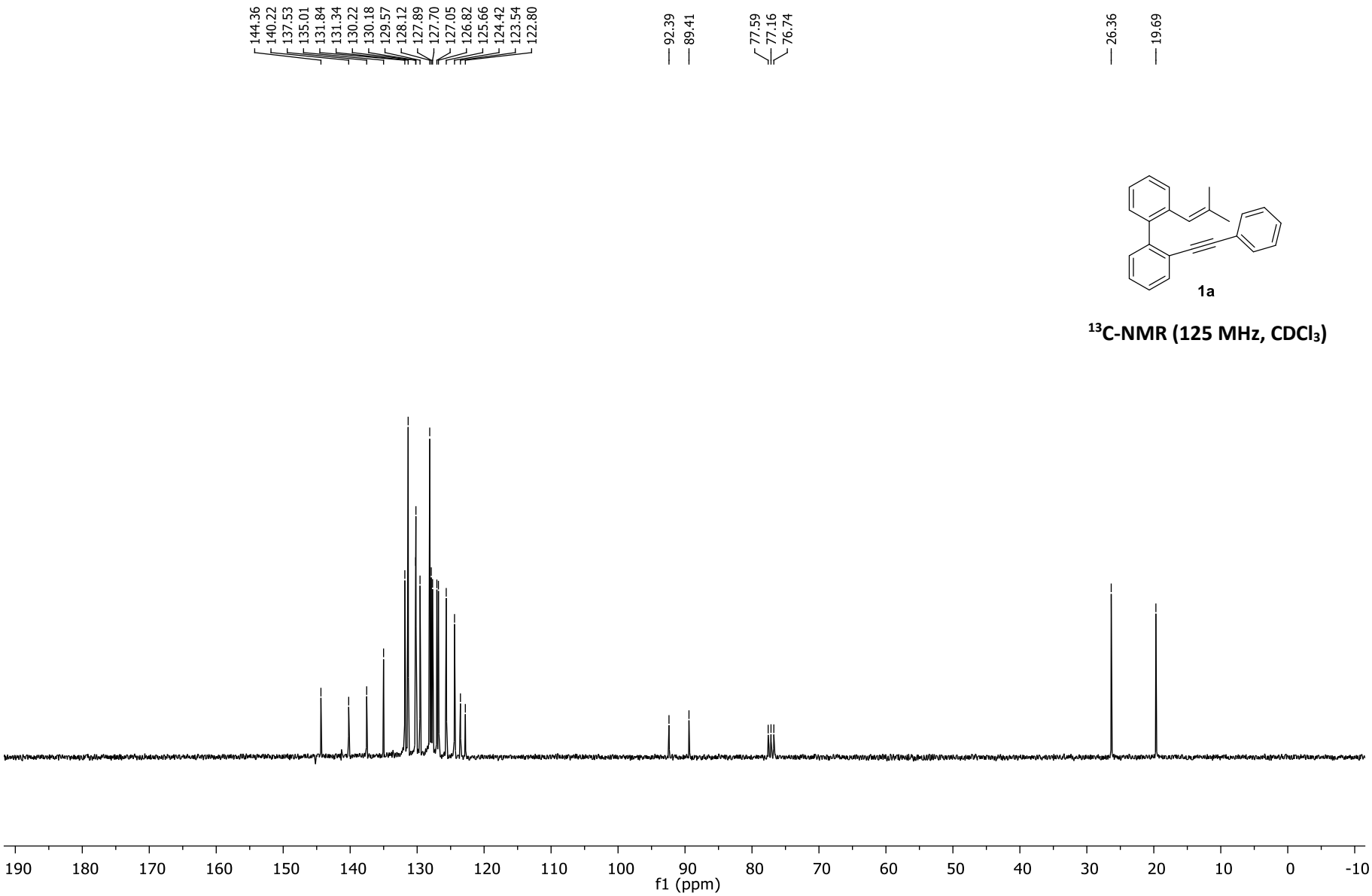


^{13}C-NMR (75 MHz, $CDCl_3$)



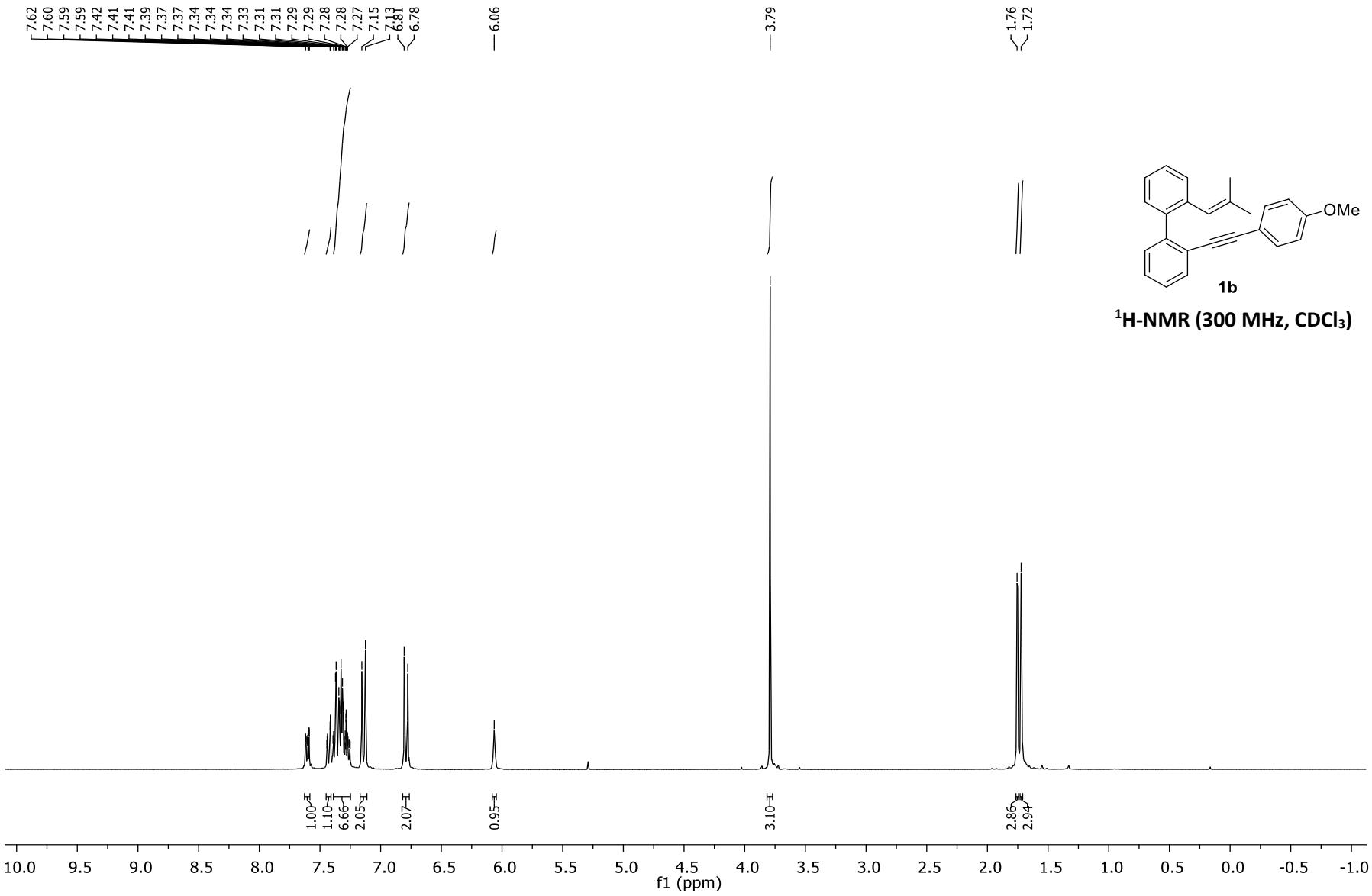
1a

^{1}H-NMR (500 MHz, $CDCl_3$)

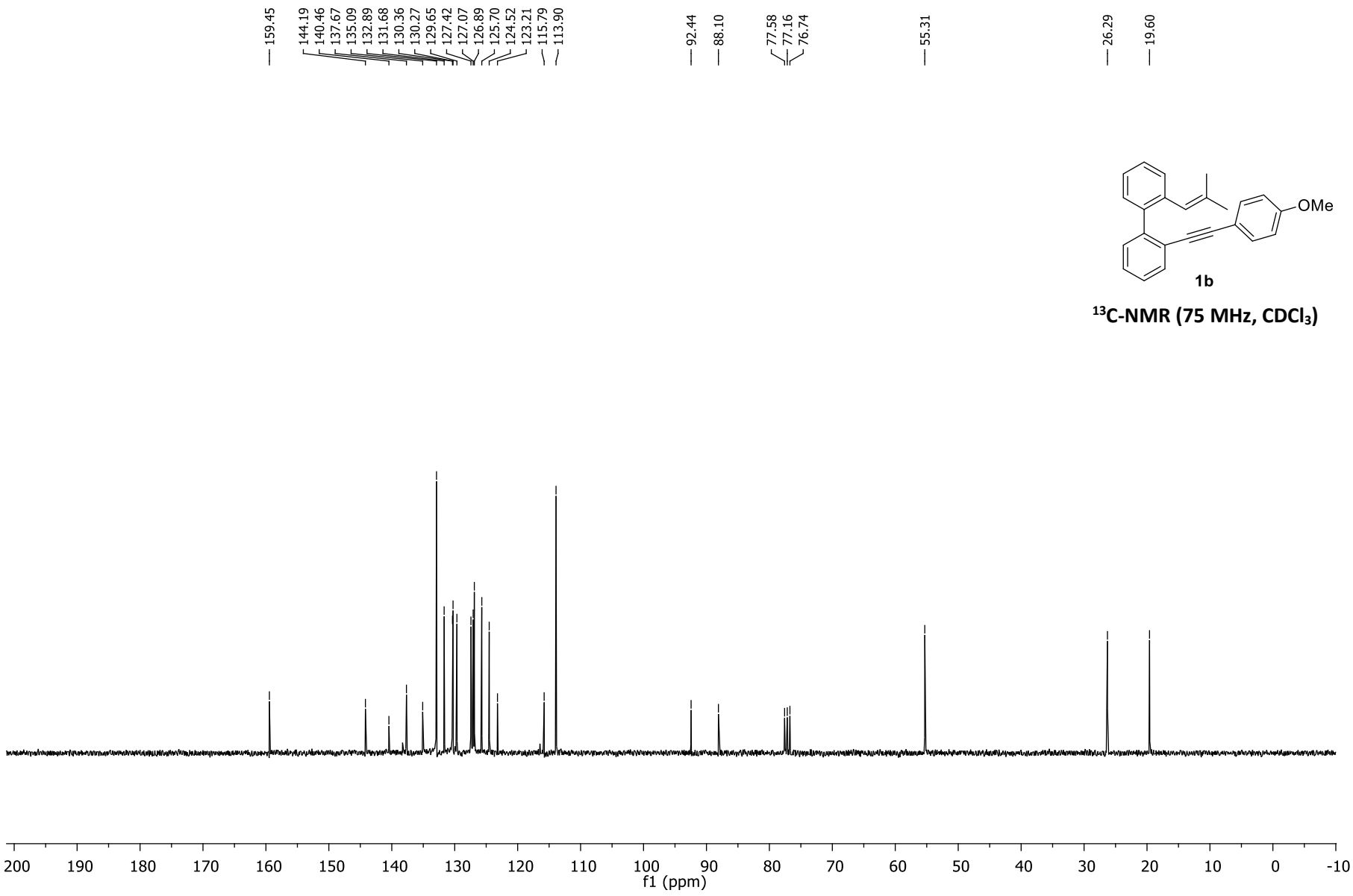


1a

^{13}C-NMR (125 MHz, $CDCl_3$)

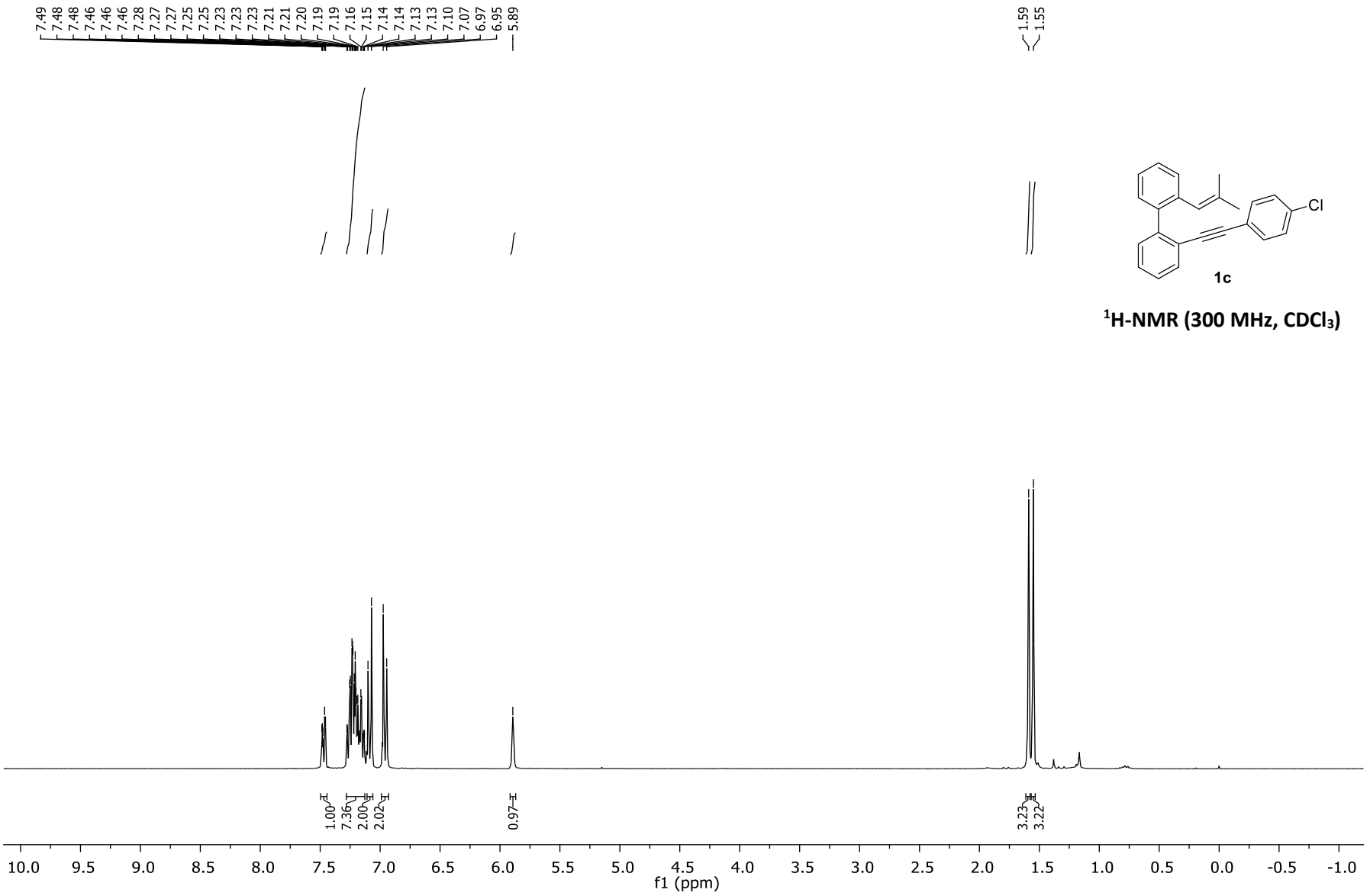


^{1}H-NMR (300 MHz, $CDCl_3$)

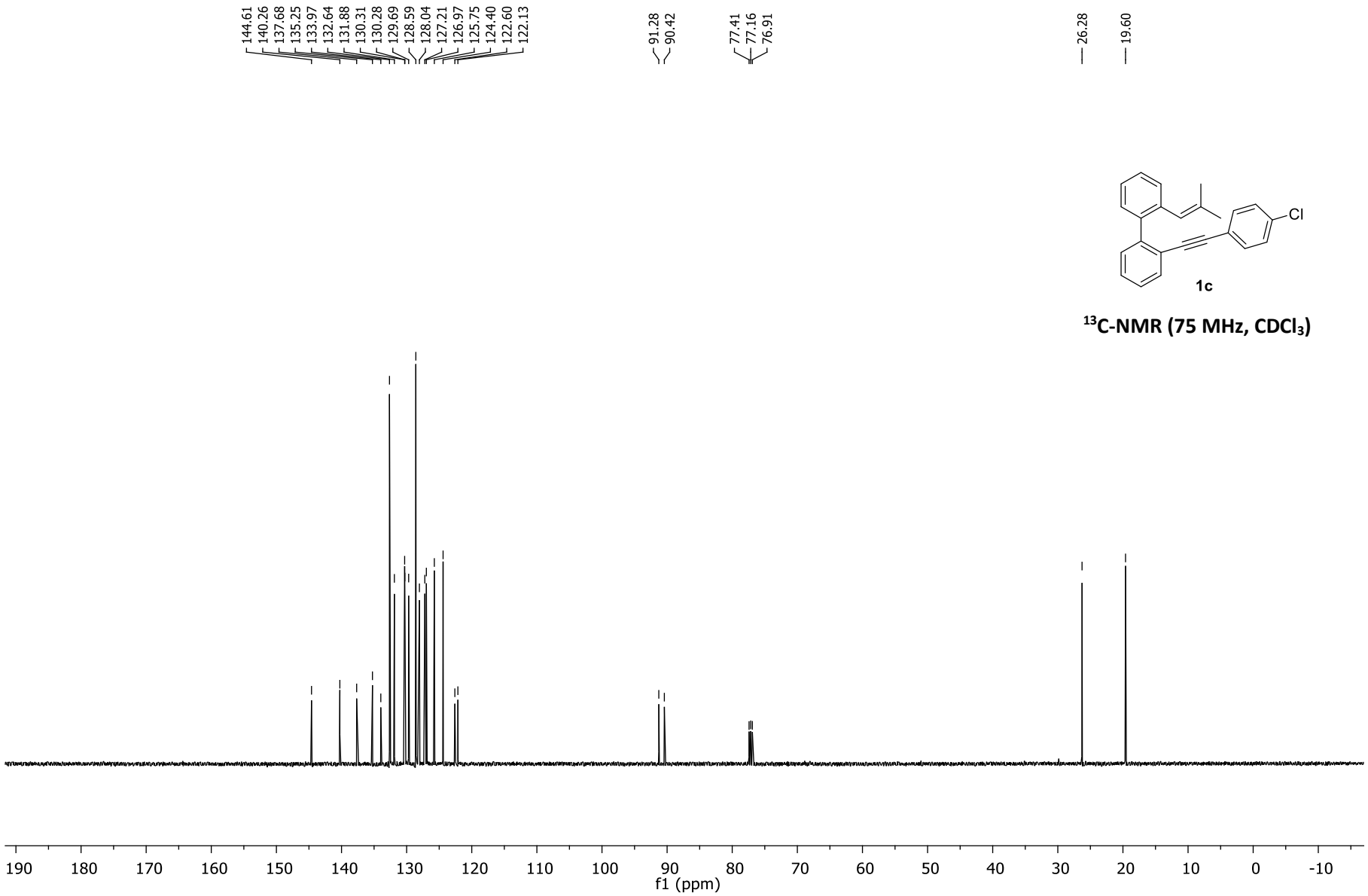


1b

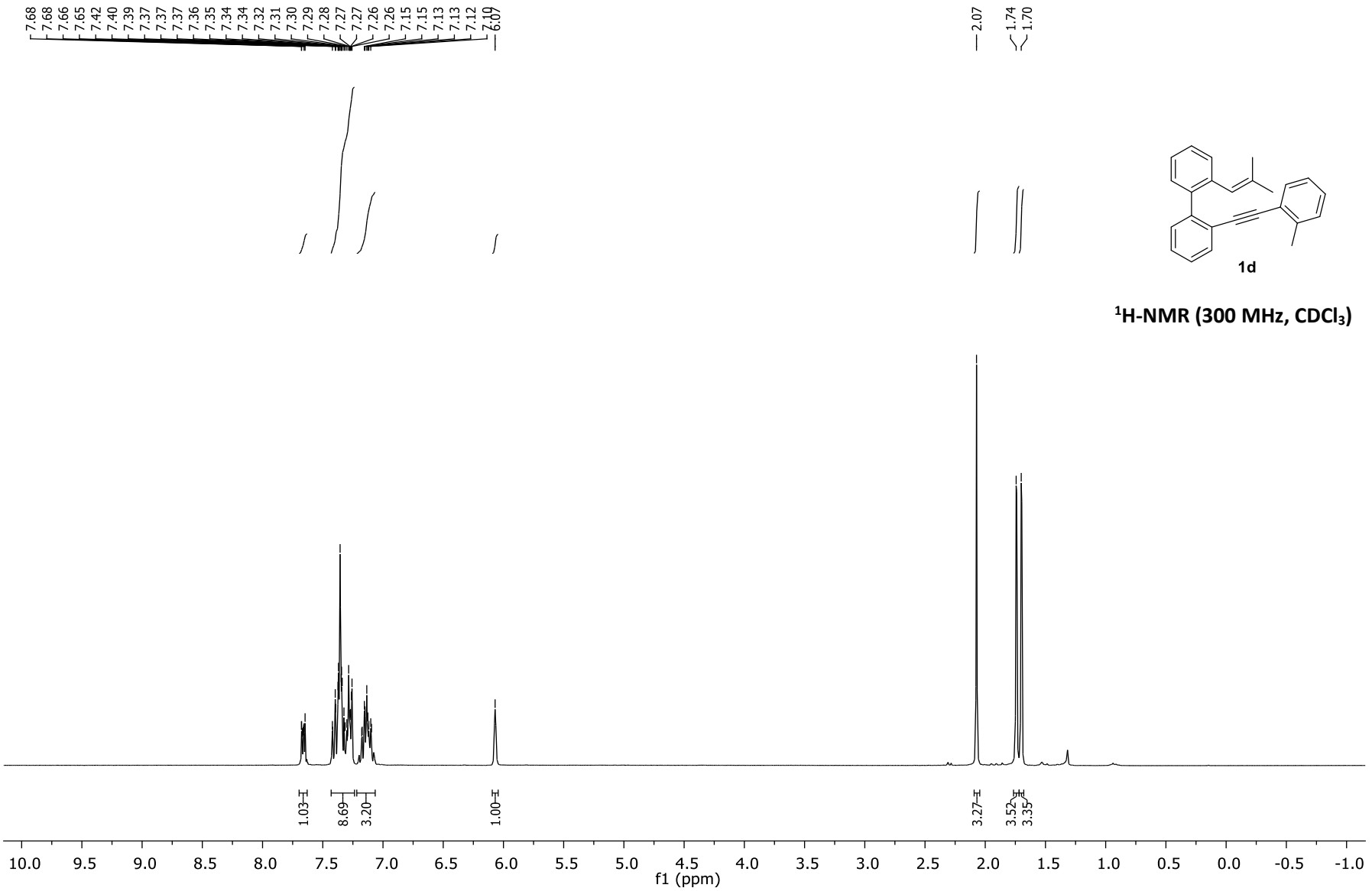
^{13}C-NMR (75 MHz, $CDCl_3$)



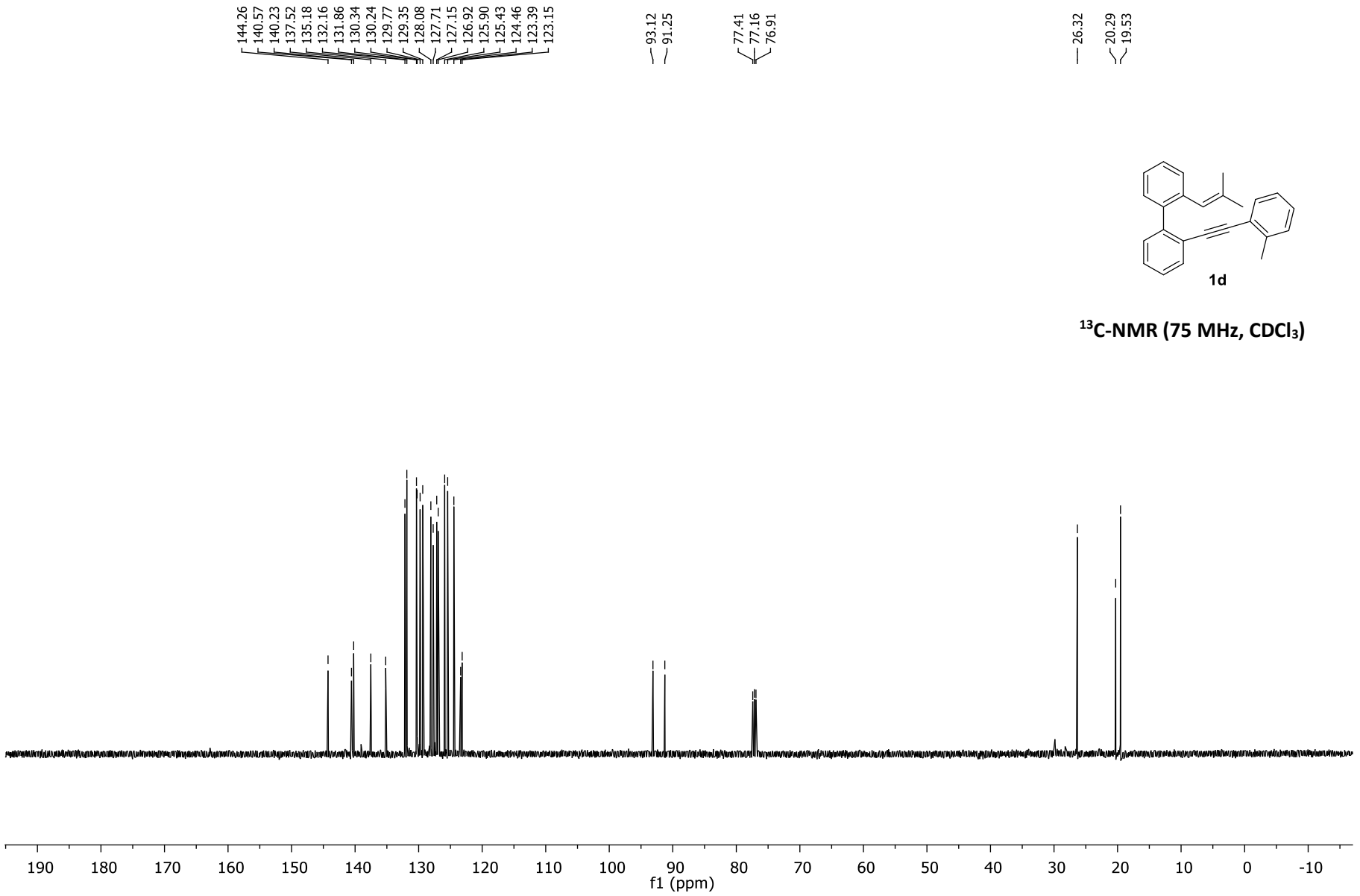
^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (75 MHz, $CDCl_3$)

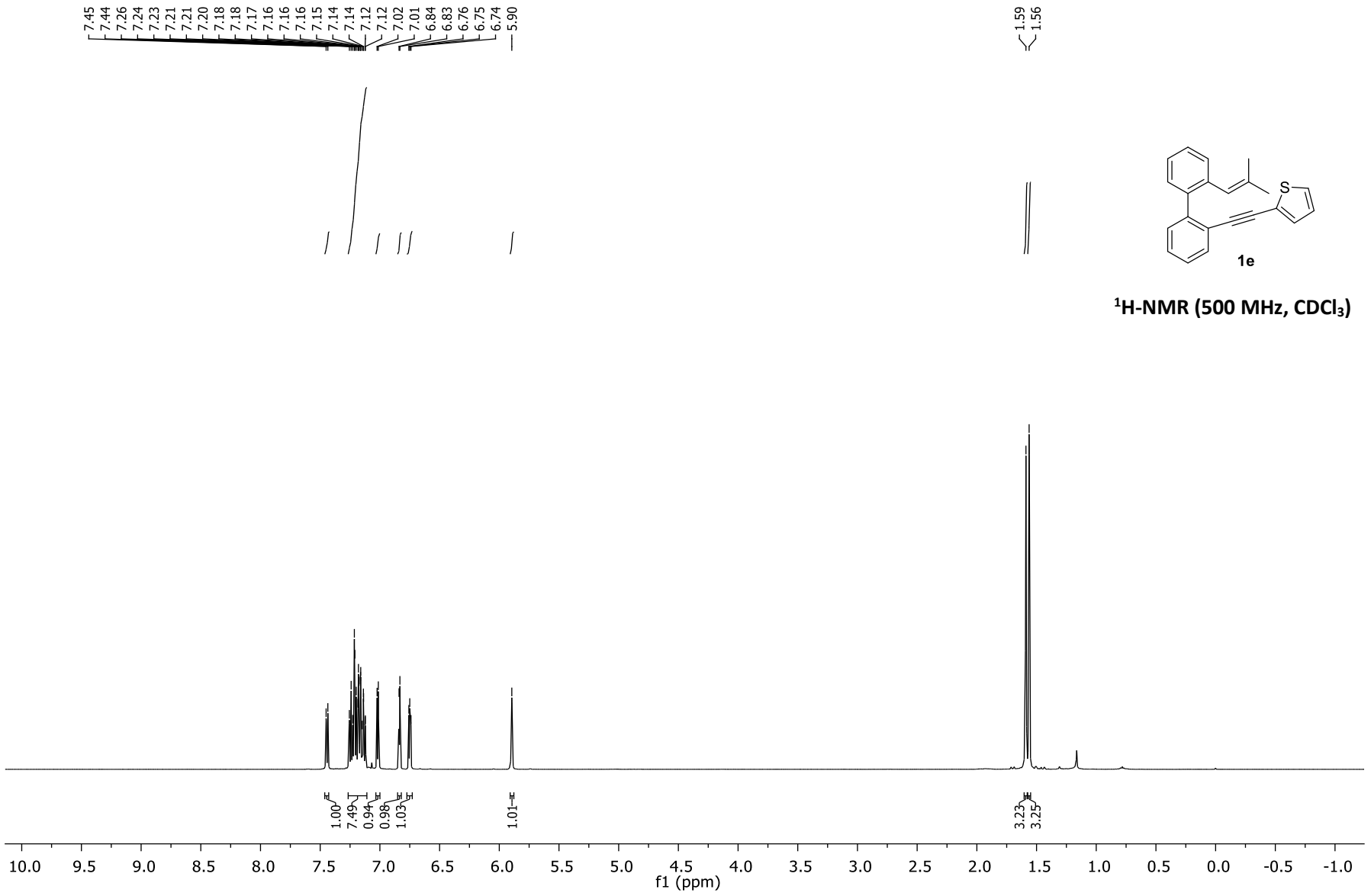


^{1}H-NMR (300 MHz, $CDCl_3$)

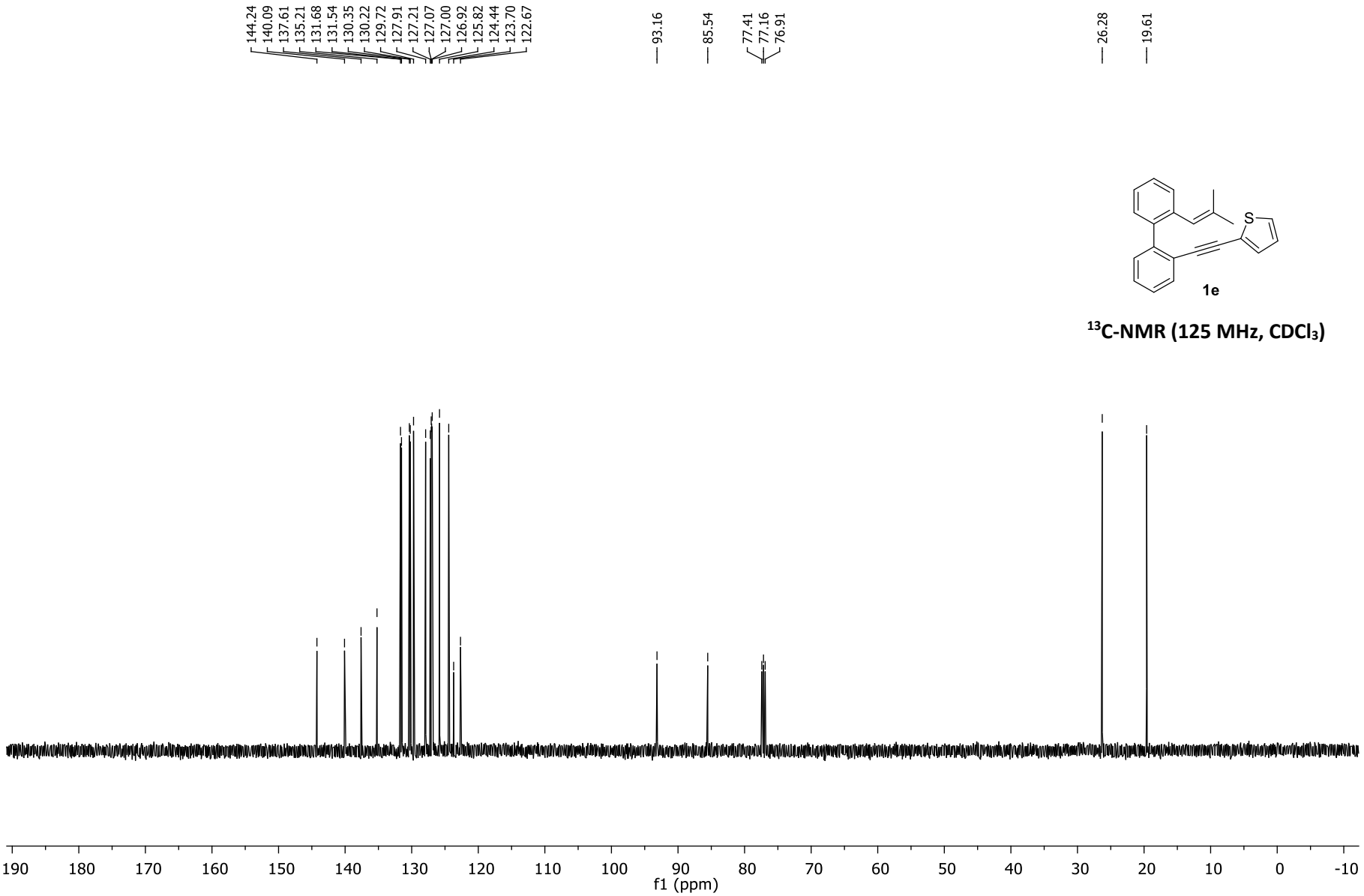


1d

^{13}C-NMR (75 MHz, $CDCl_3$)

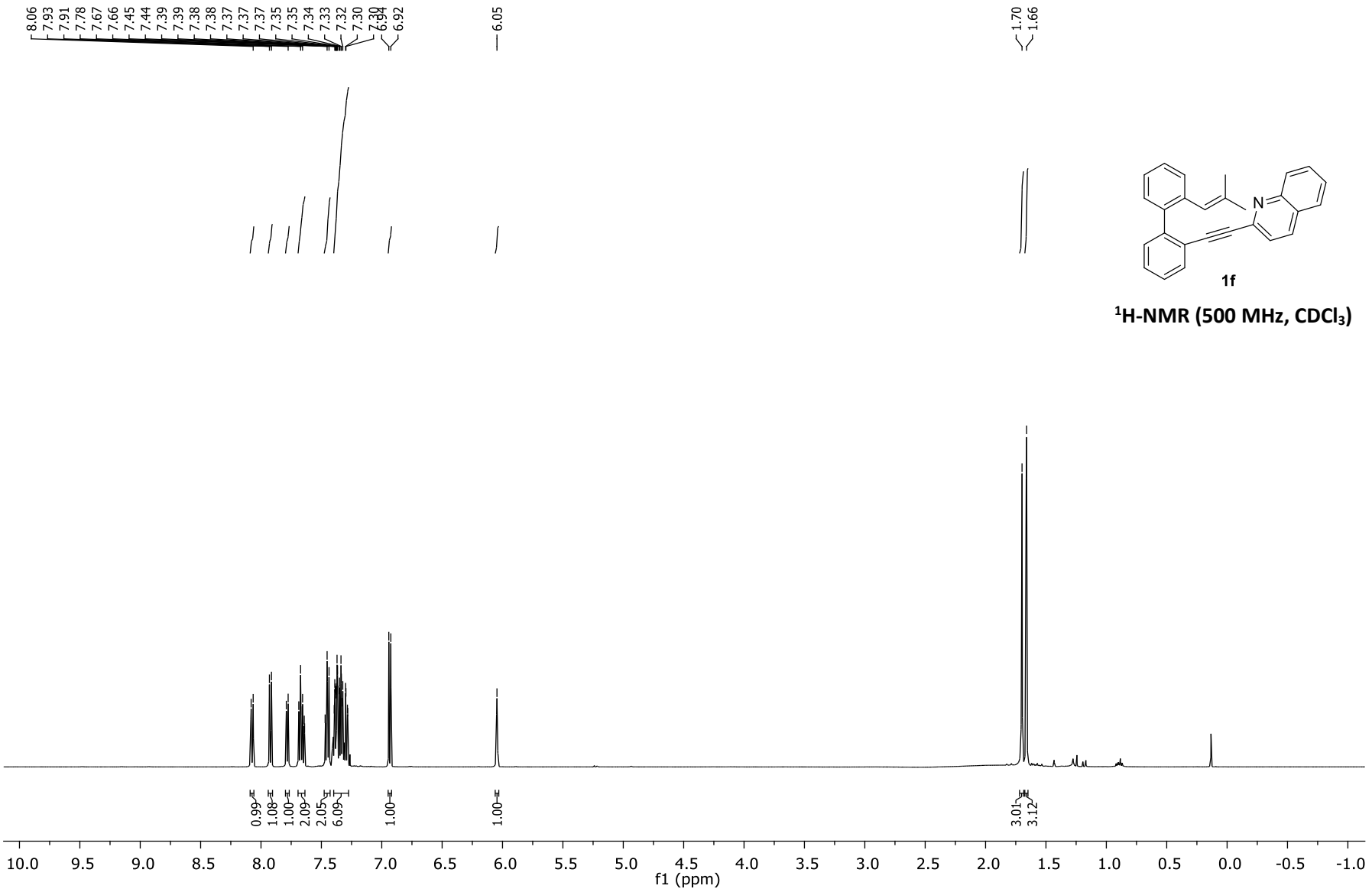


^{1}H-NMR (500 MHz, $CDCl_3$)



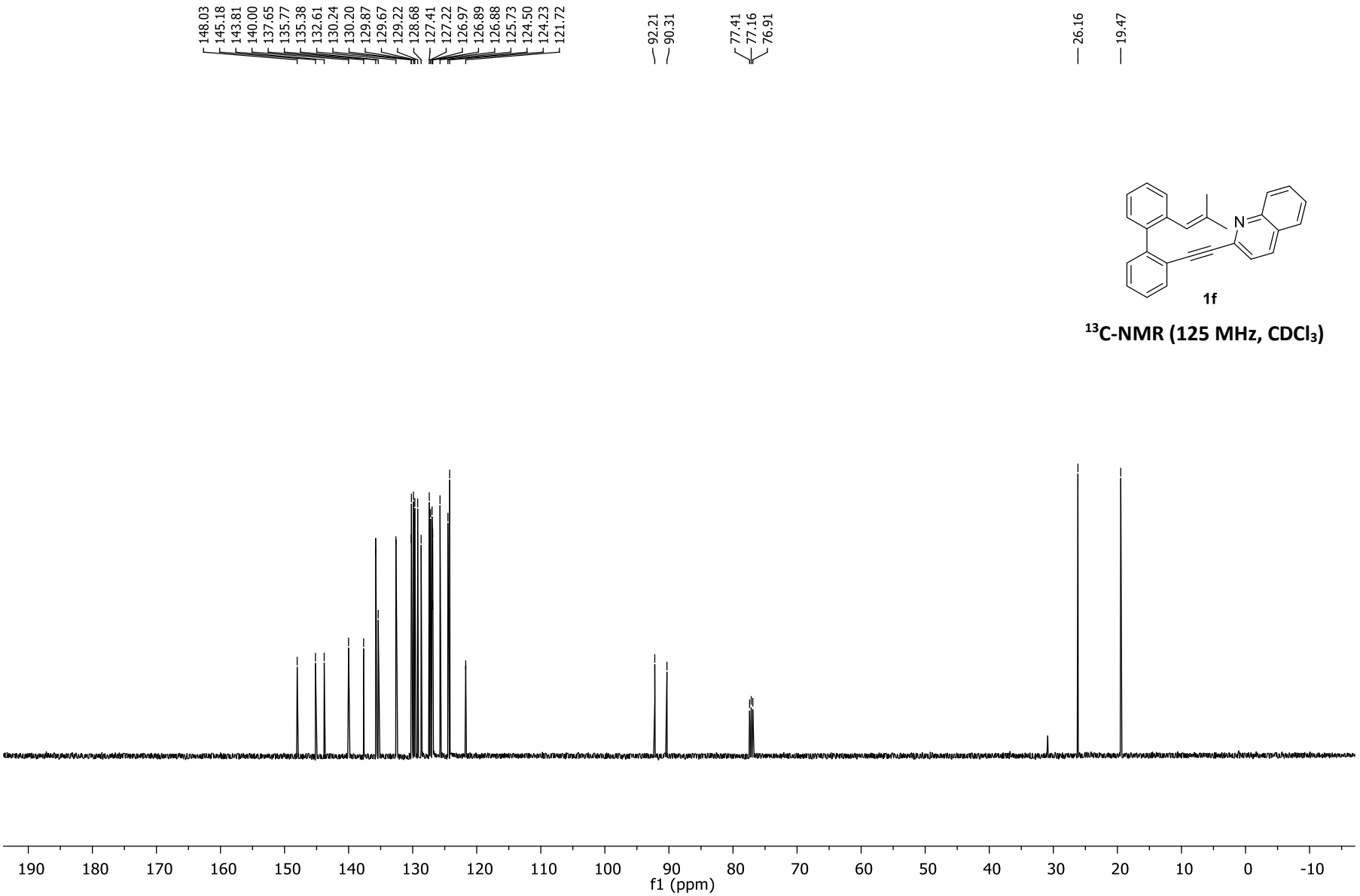
1e

^{13}C-NMR (125 MHz, $CDCl_3$)

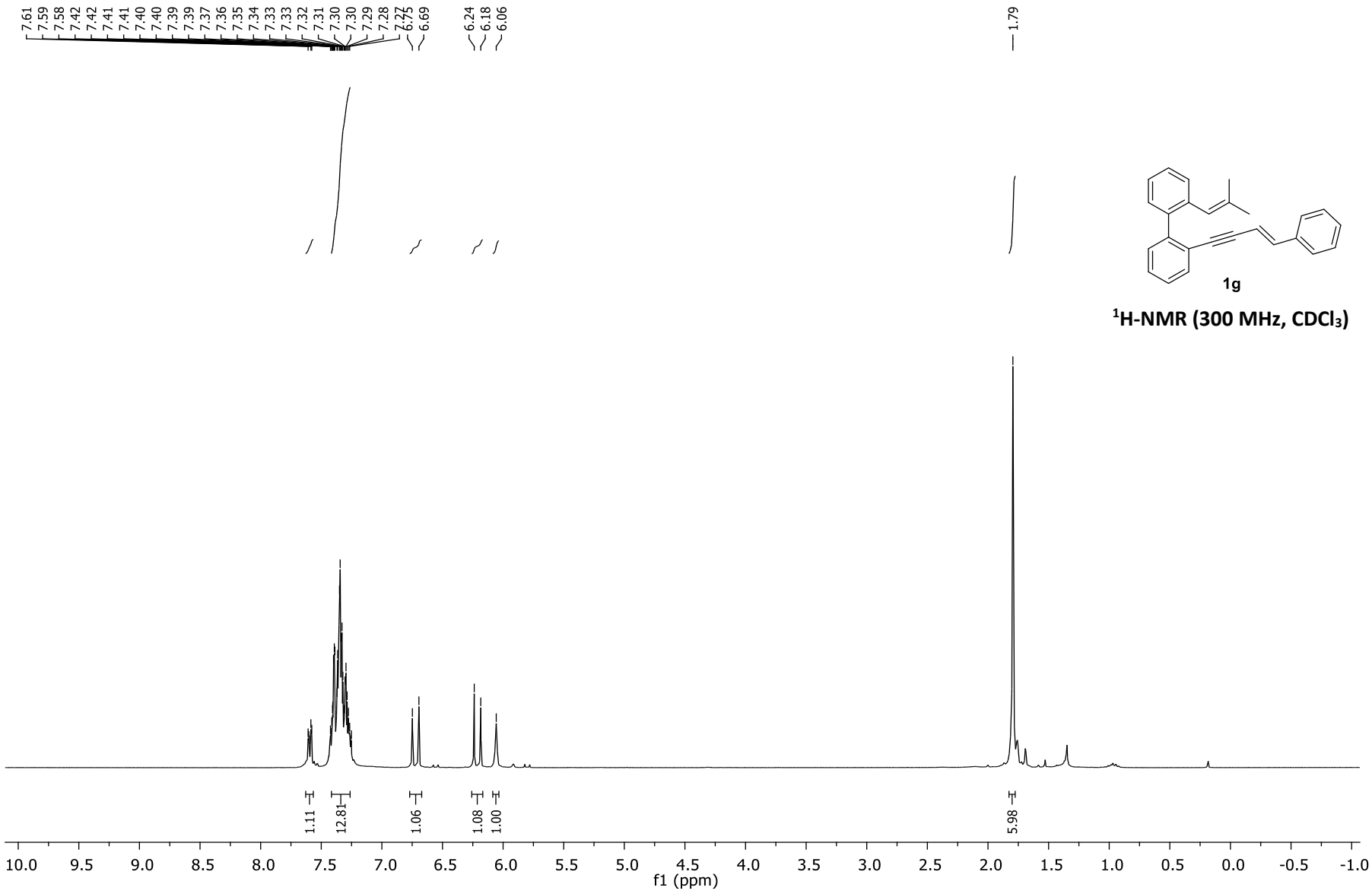


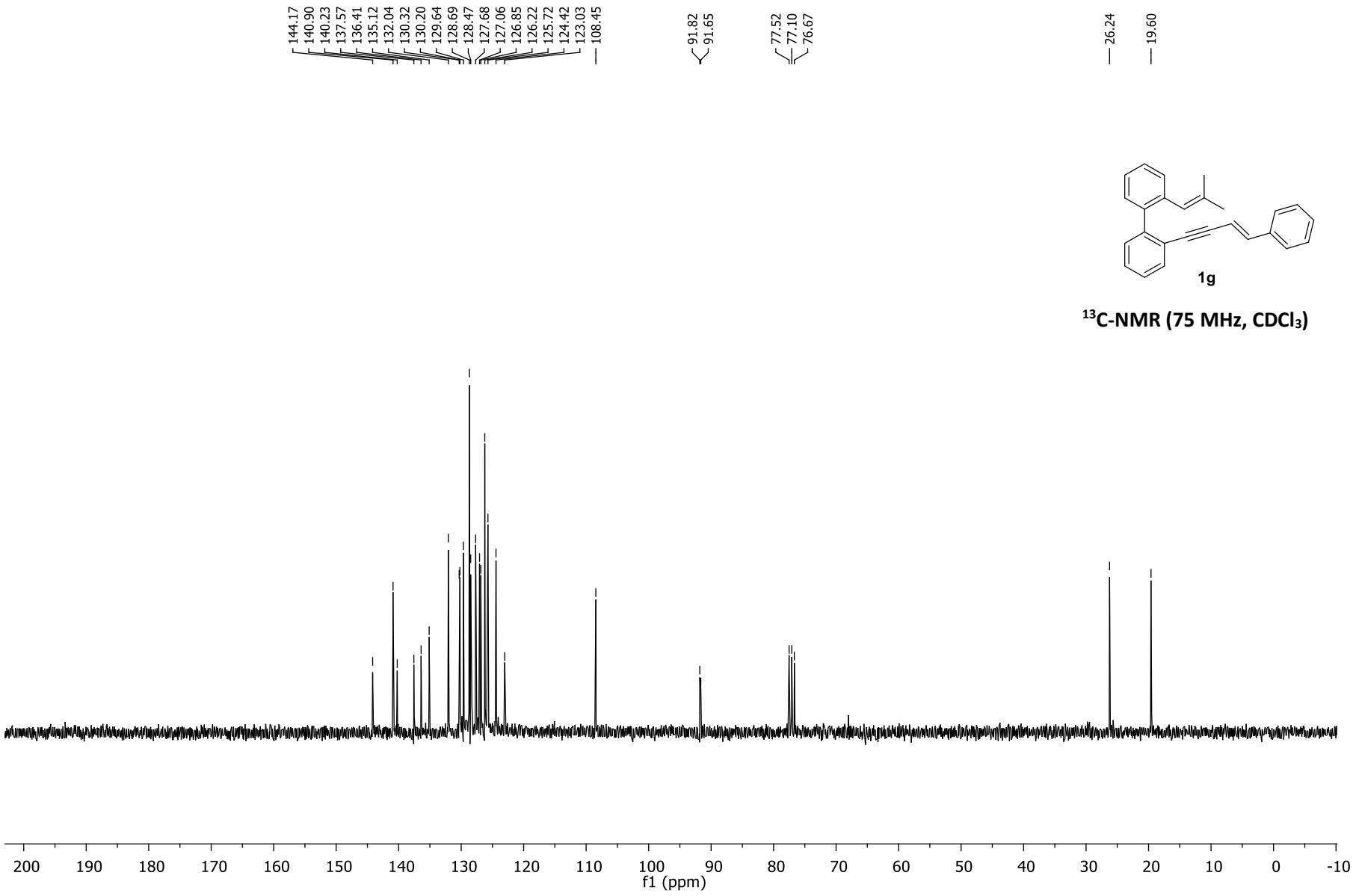
1f

^{1}H-NMR (500 MHz, $CDCl_3$)



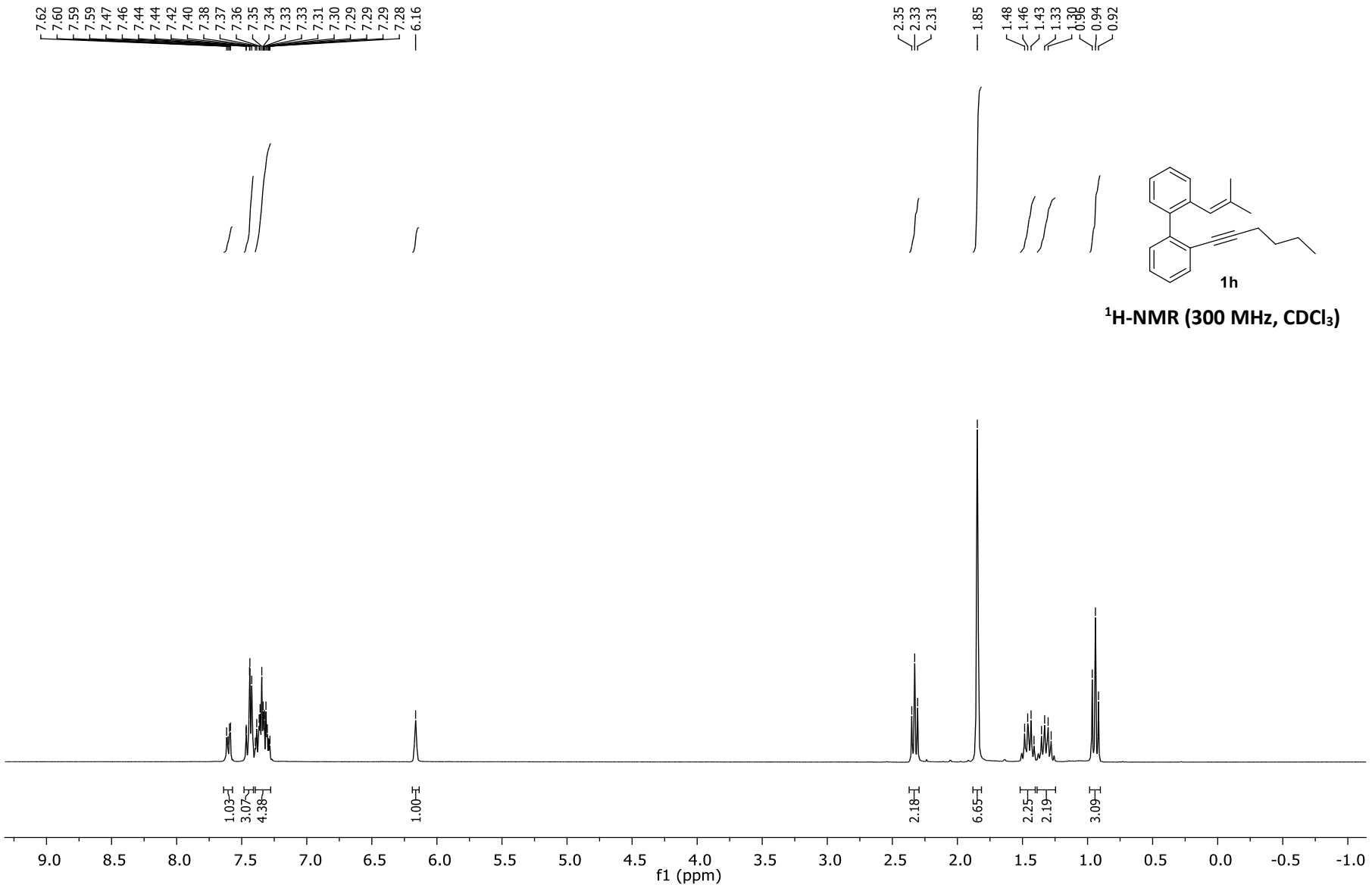
^{13}C-NMR (125 MHz, $CDCl_3$)


7.61
7.59
7.58
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
6.69
6.24
6.18
6.06
1.79
1g
1H-NMR (300 MHz, CDCl3)
1.11
12.81
1.06
1.08
1.00
5.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

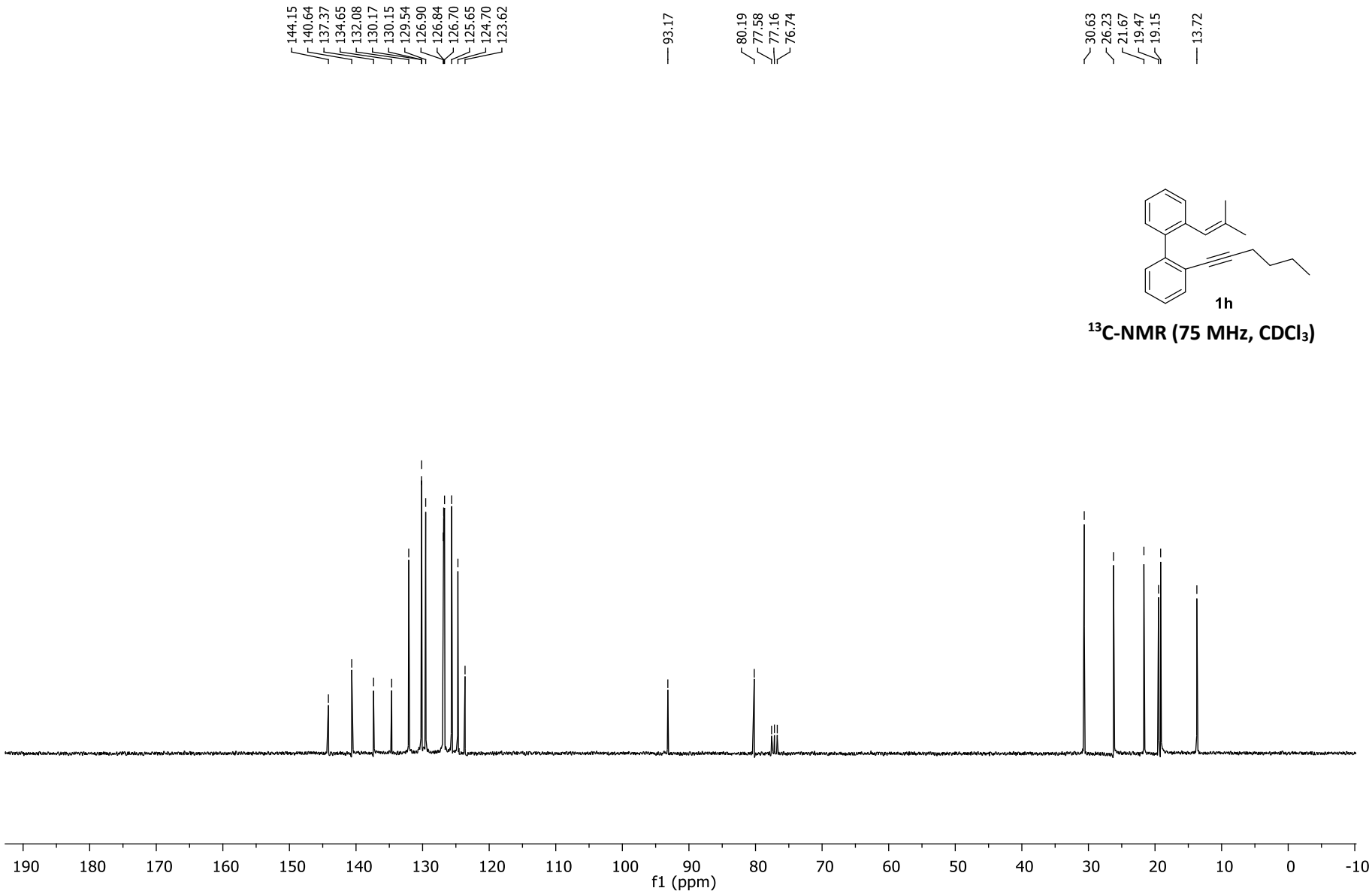


1g

^{13}C-NMR (75 MHz, $CDCl_3$)

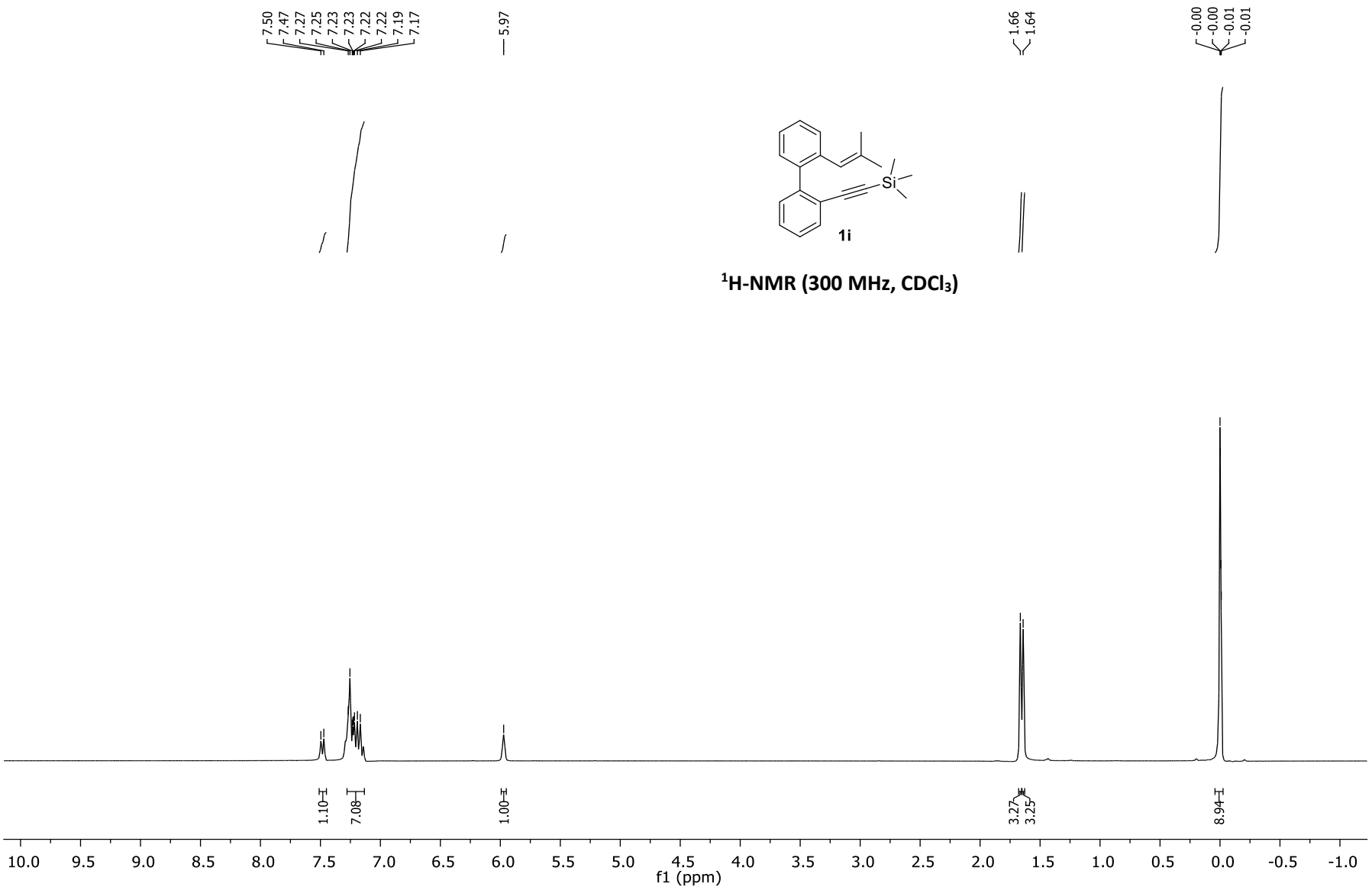


^{1}H-NMR (300 MHz, $CDCl_3$)

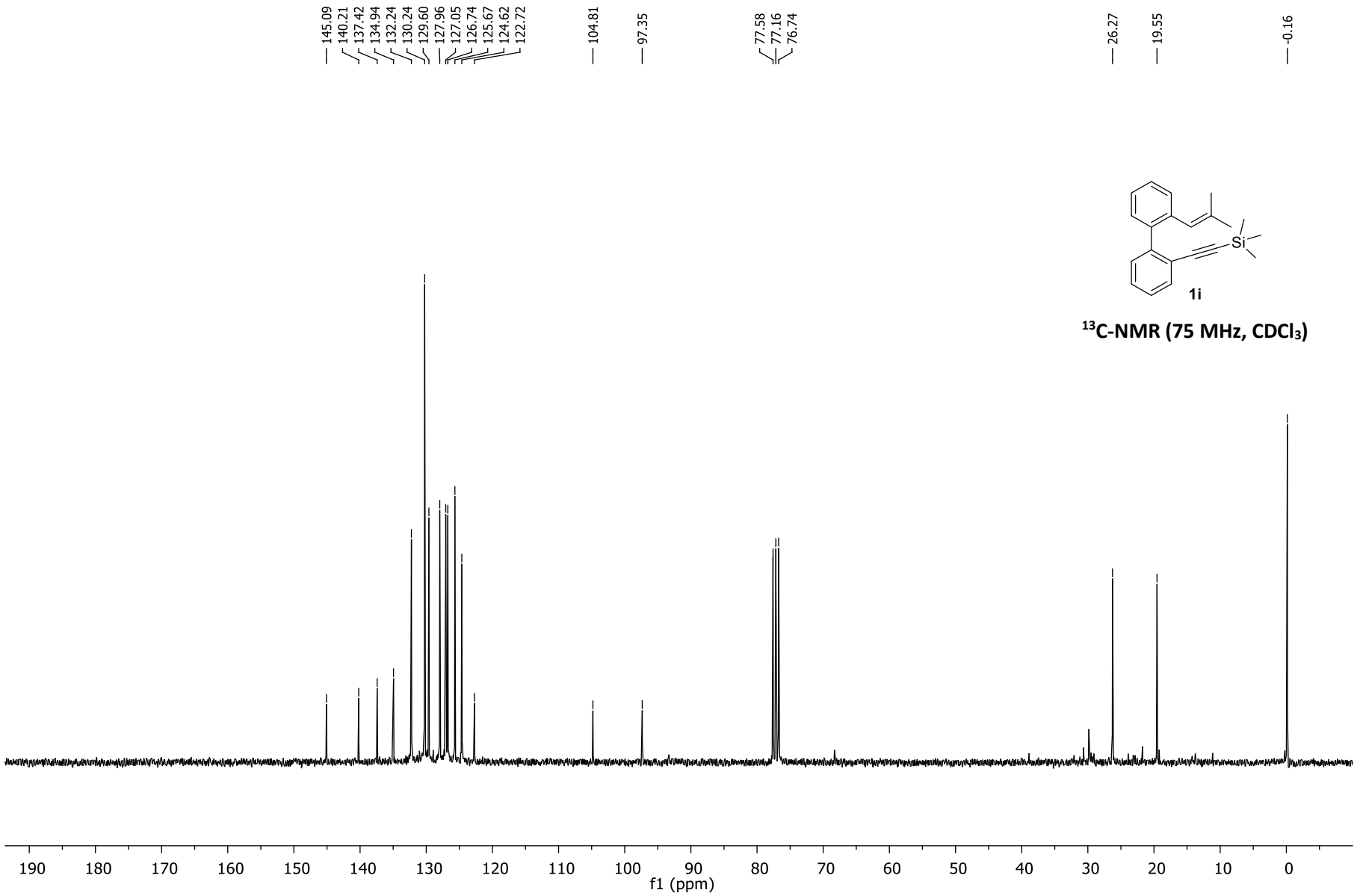


1h

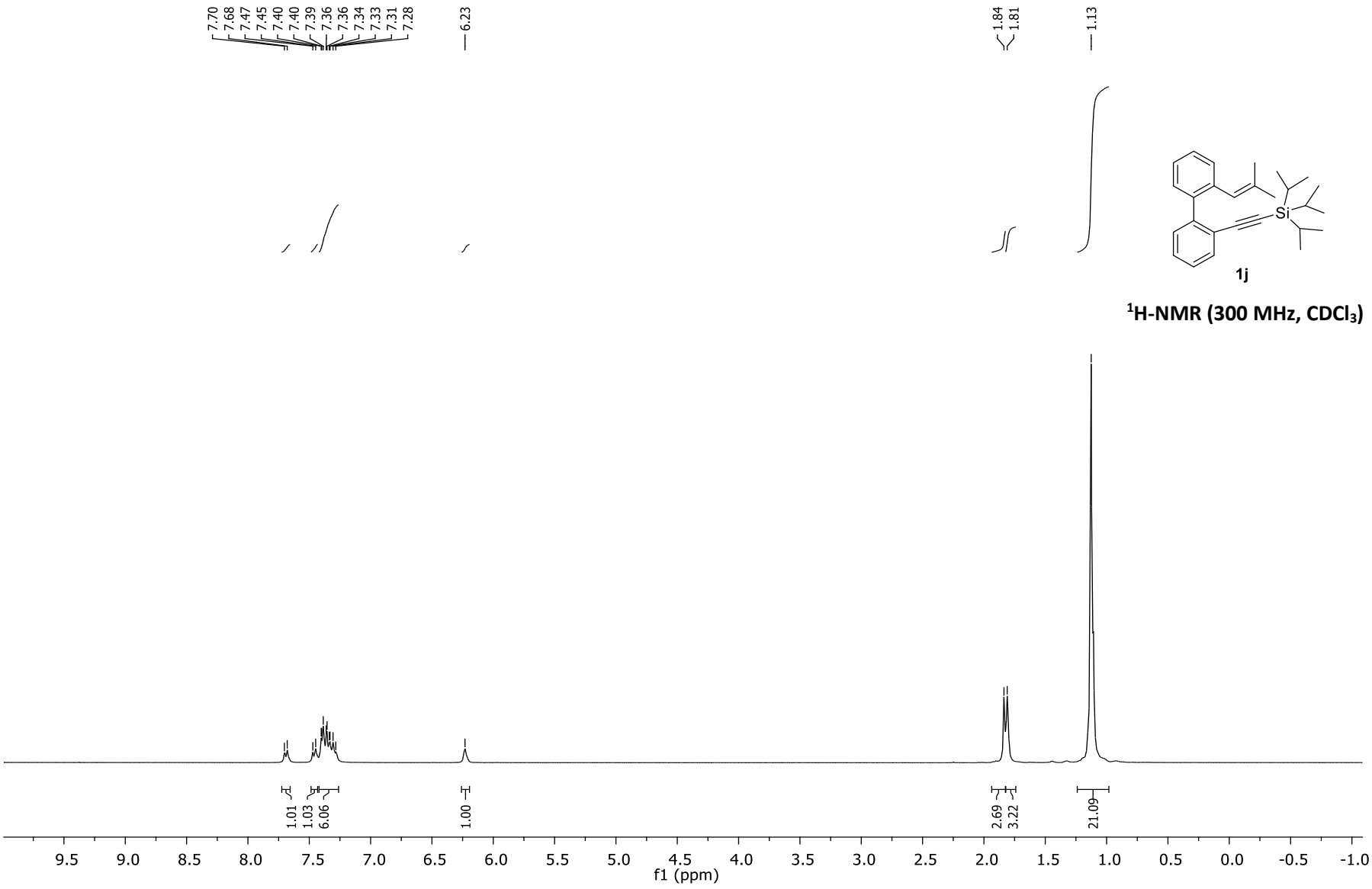
^{13}C-NMR (75 MHz, $CDCl_3$)



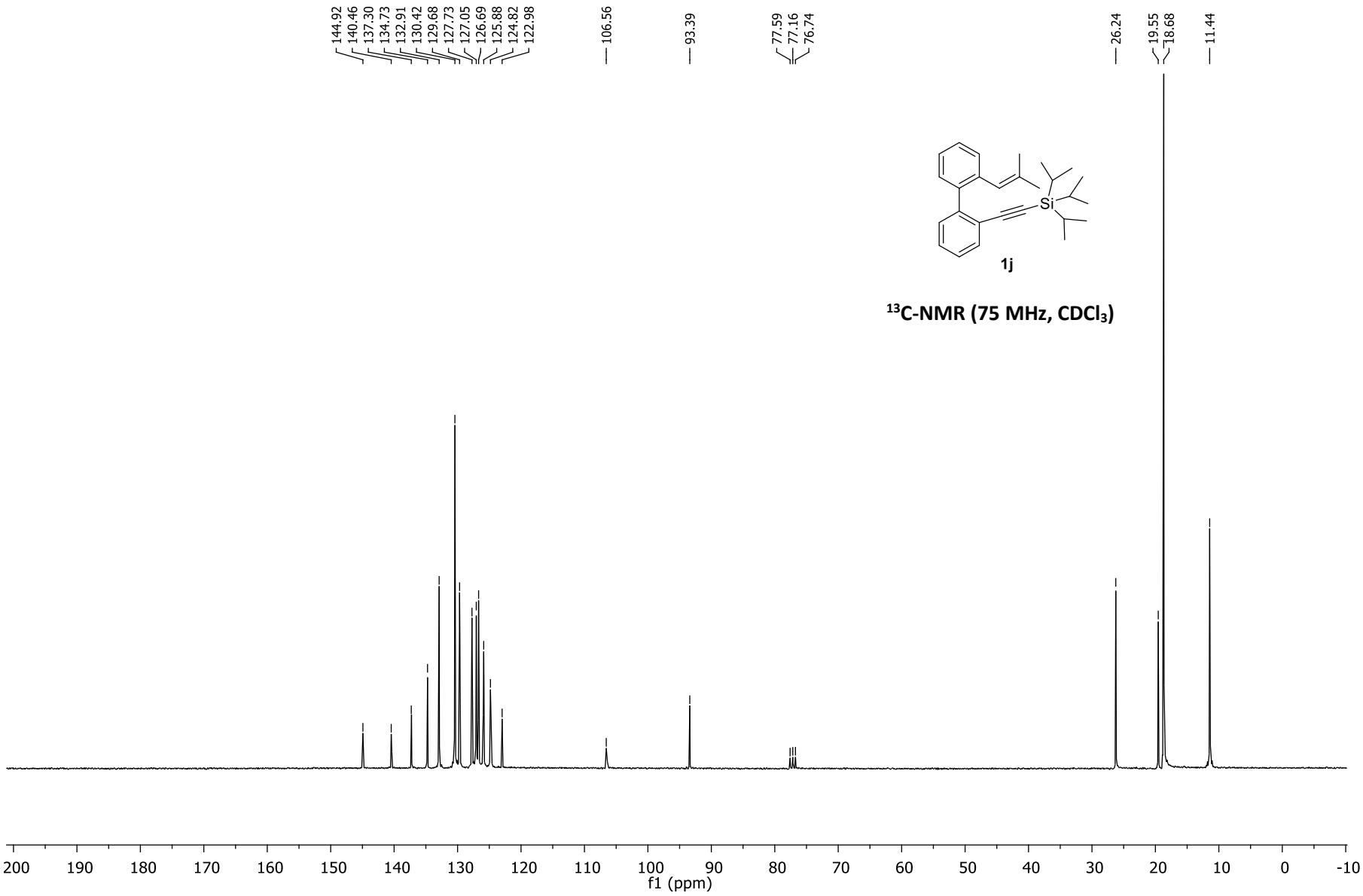
^{1}H-NMR (300 MHz, $CDCl_3$)

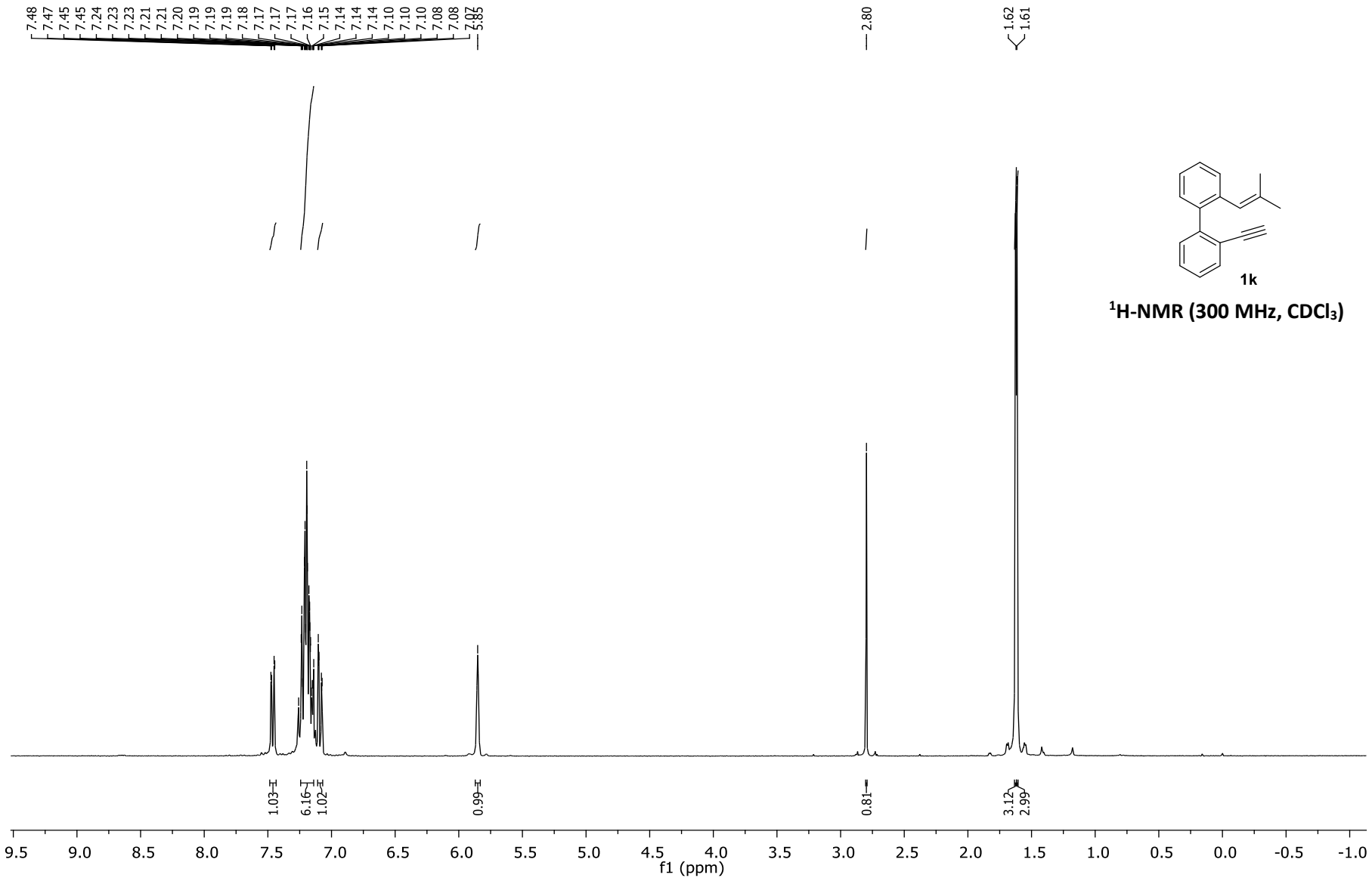


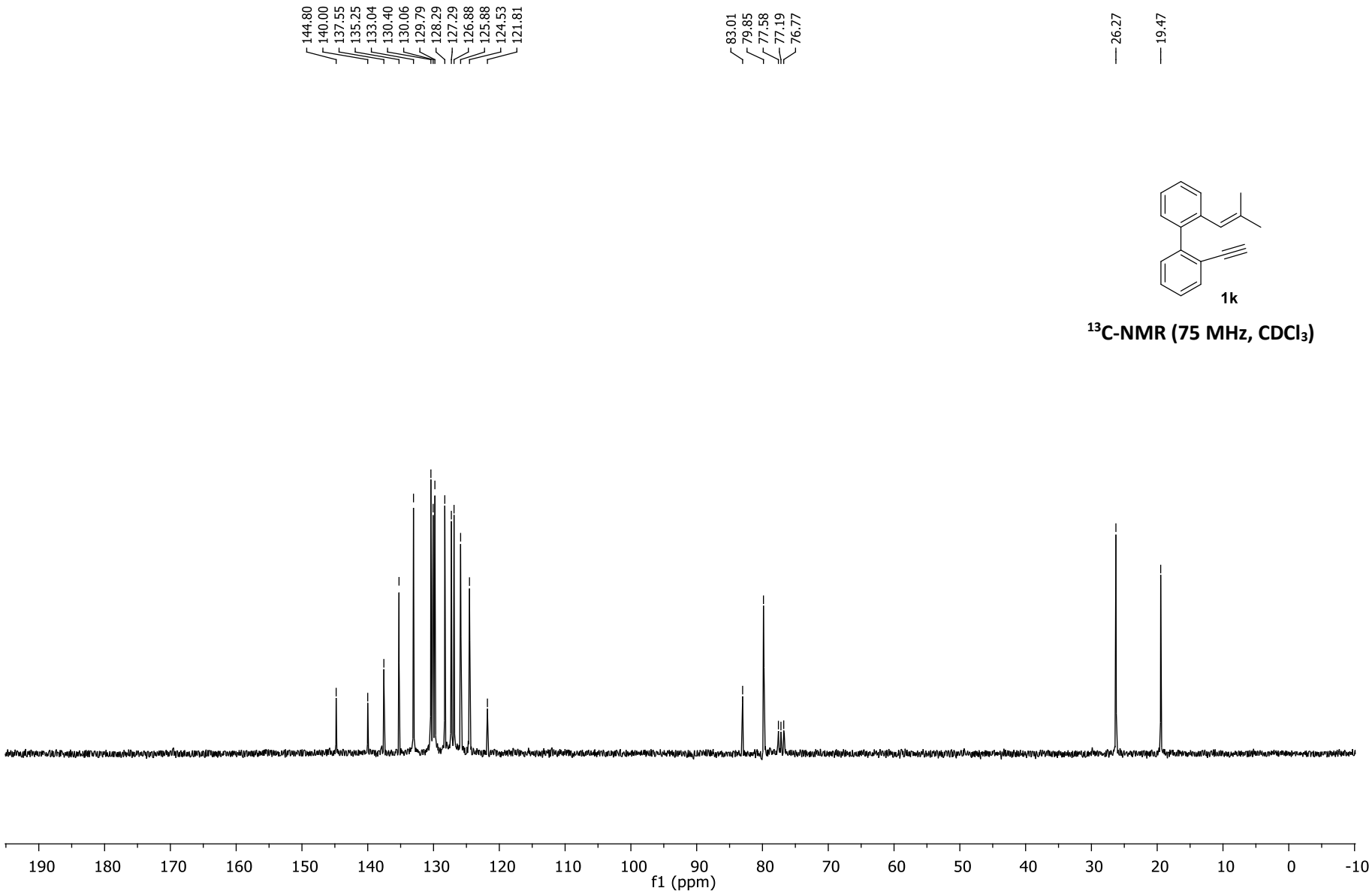
^{13}C-NMR (75 MHz, $CDCl_3$)



^{1}H-NMR (300 MHz, $CDCl_3$)

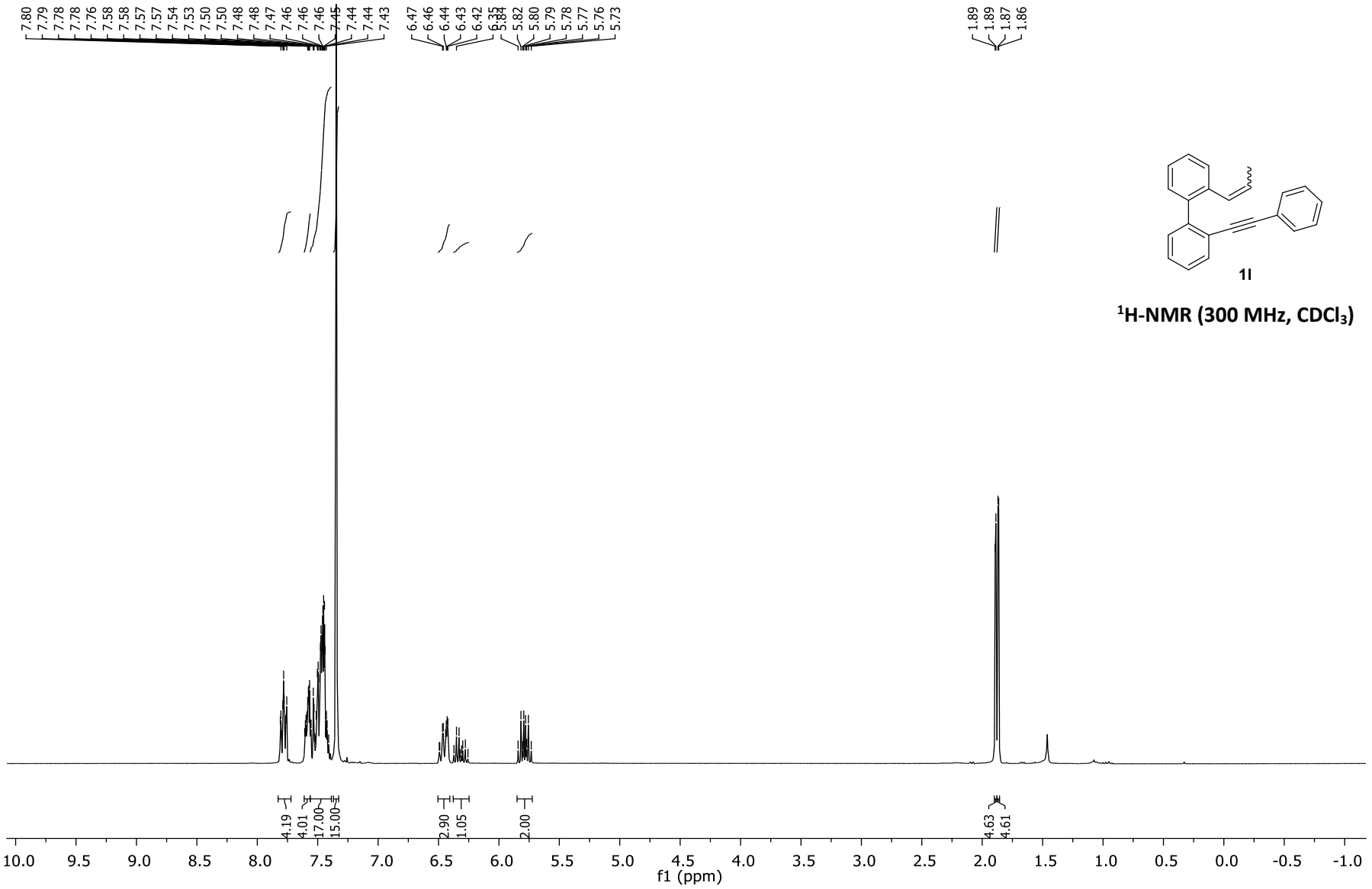

144.92
140.46
137.30
134.73
132.91
130.42
129.68
127.73
127.05
126.69
125.88
124.82
122.98
106.56
93.39
77.59
77.16
76.74
26.24
19.55
18.68
11.44
Si
1j
13C-NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.48
7.47
7.45
7.45
7.24
7.23
7.23
7.21
7.21
7.20
7.19
7.19
7.19
7.18
7.17
7.17
7.17
7.16
7.15
7.14
7.14
7.14
7.10
7.10
7.08
7.08
7.07
5.85
2.80
1.62
1.61
1k
1H-NMR (300 MHz, CDCl3)
1.03
6.16
1.02
0.99
0.81
3.12
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



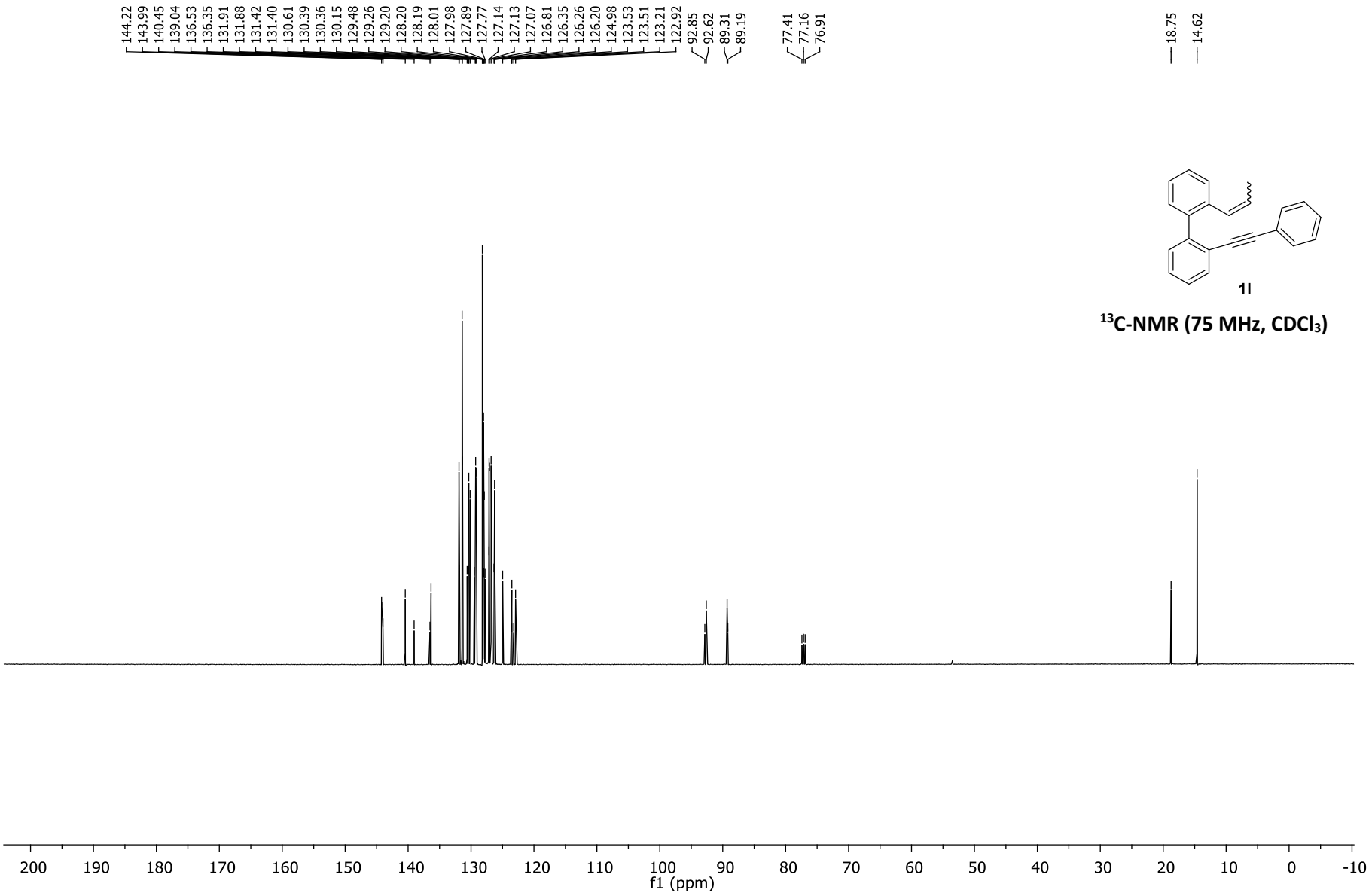
1k

^{13}C-NMR (75 MHz, $CDCl_3$)

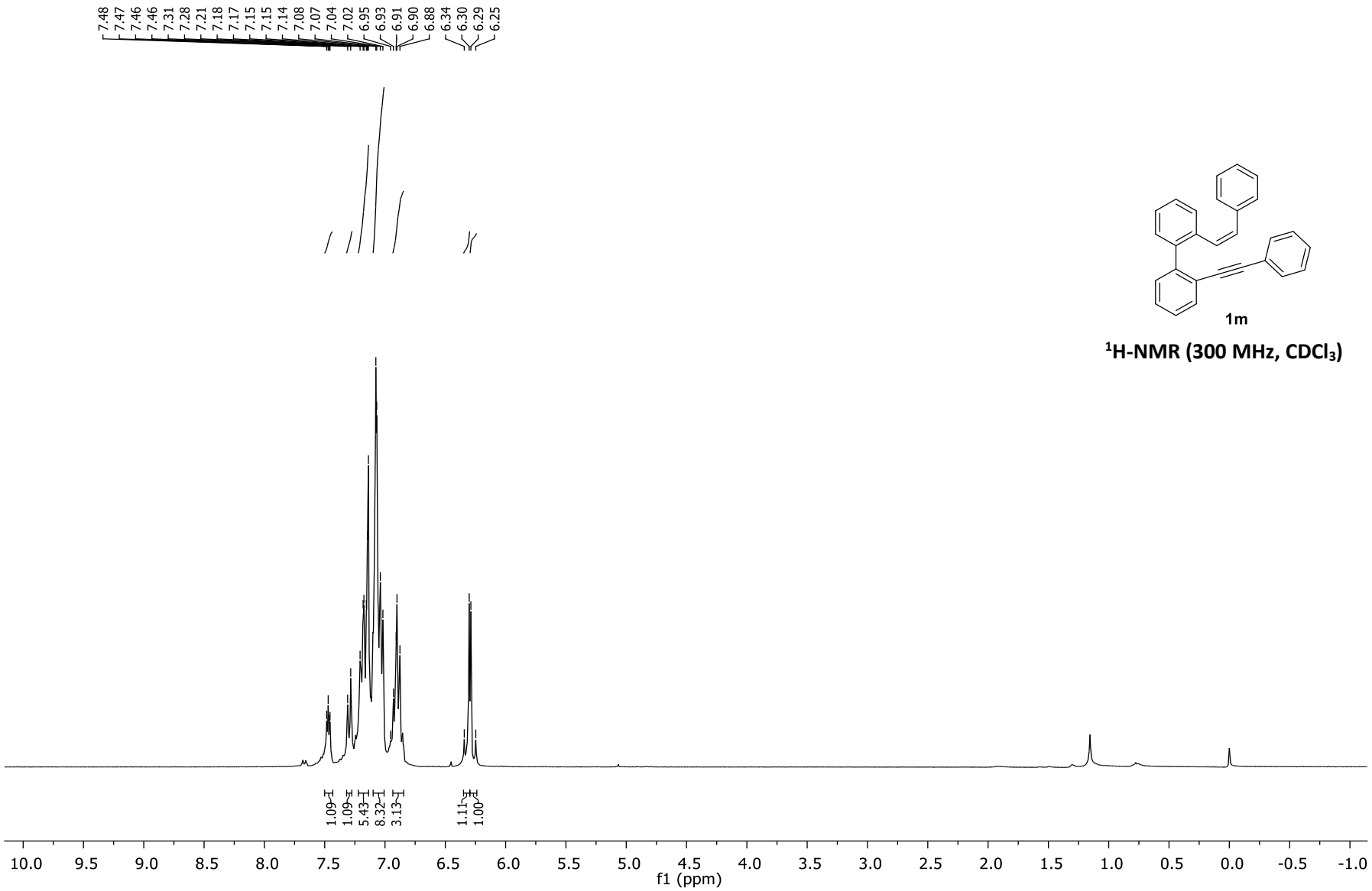


1l

^{1}H-NMR (300 MHz, $CDCl_3$)

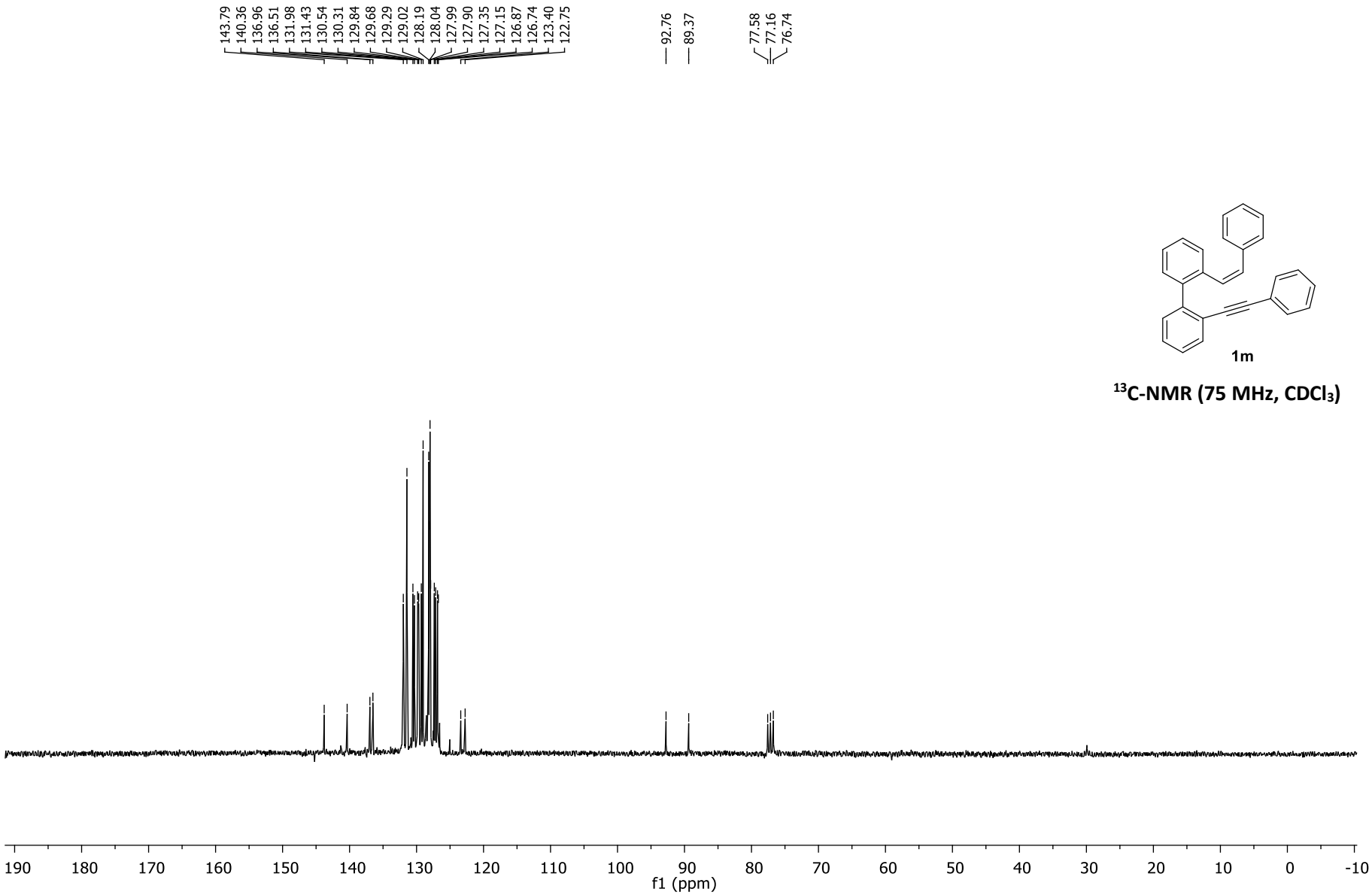


^{13}C-NMR (75 MHz, $CDCl_3$)



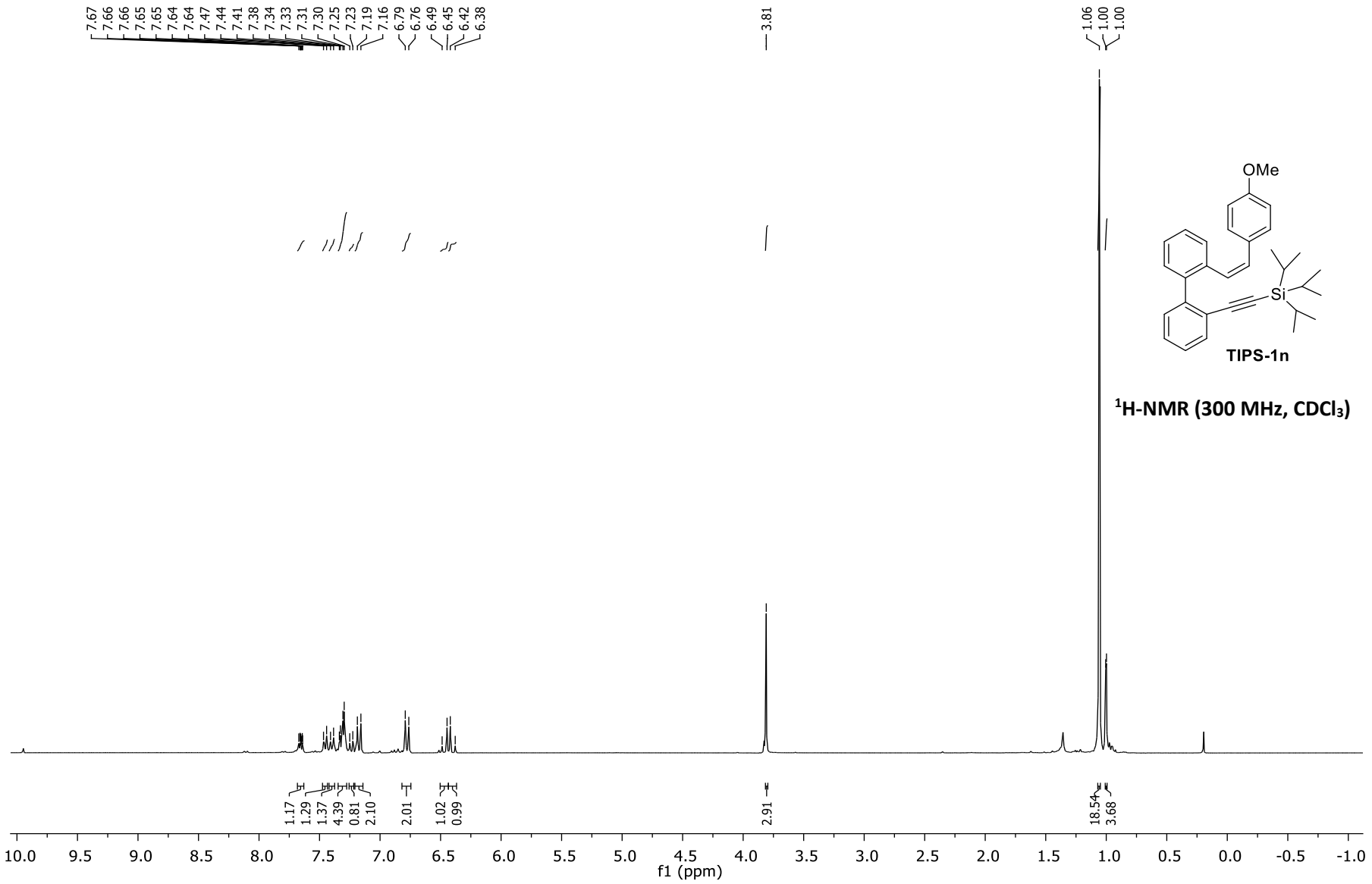
1m

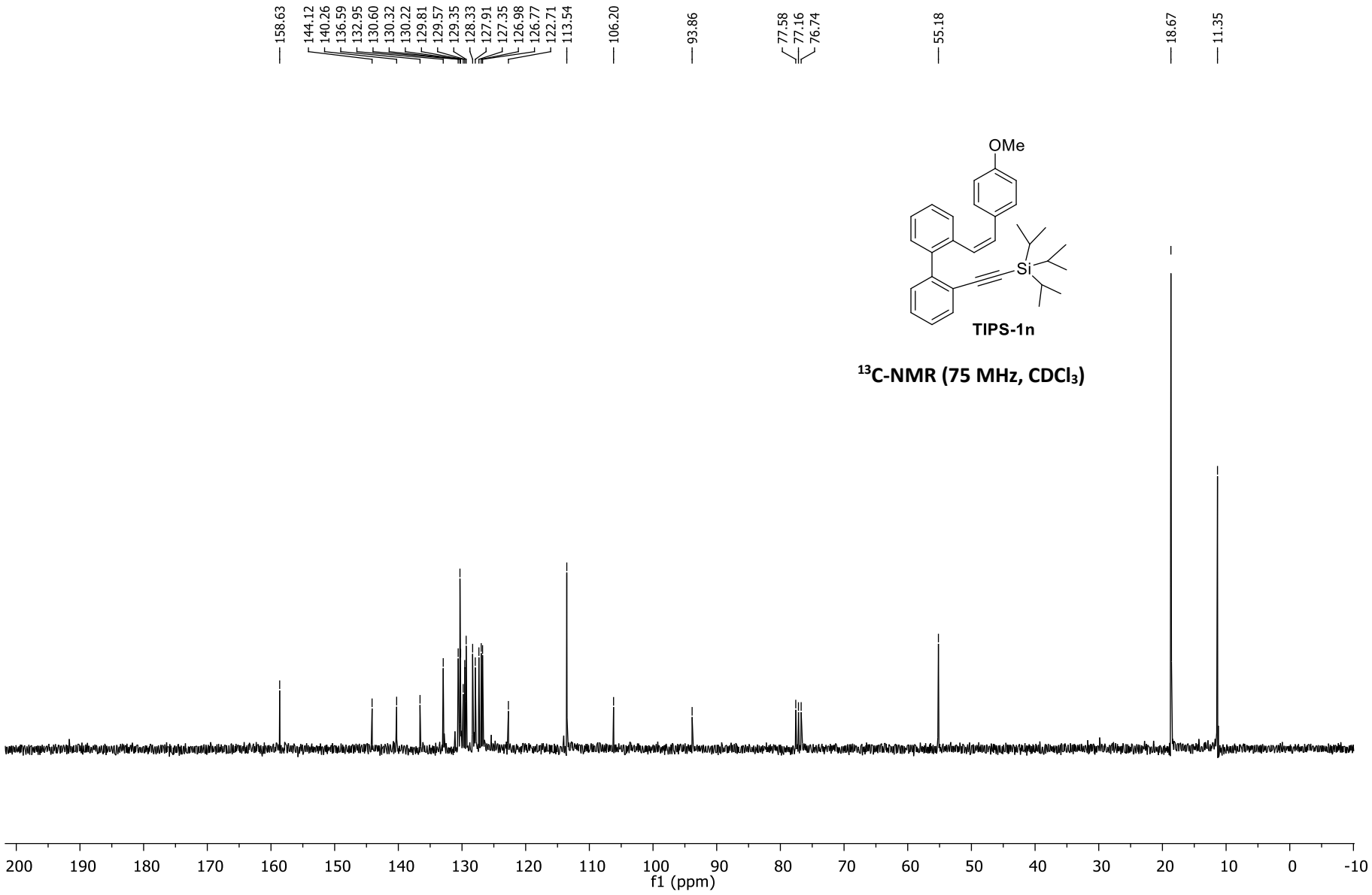
^{1}H-NMR (300 MHz, $CDCl_3$)

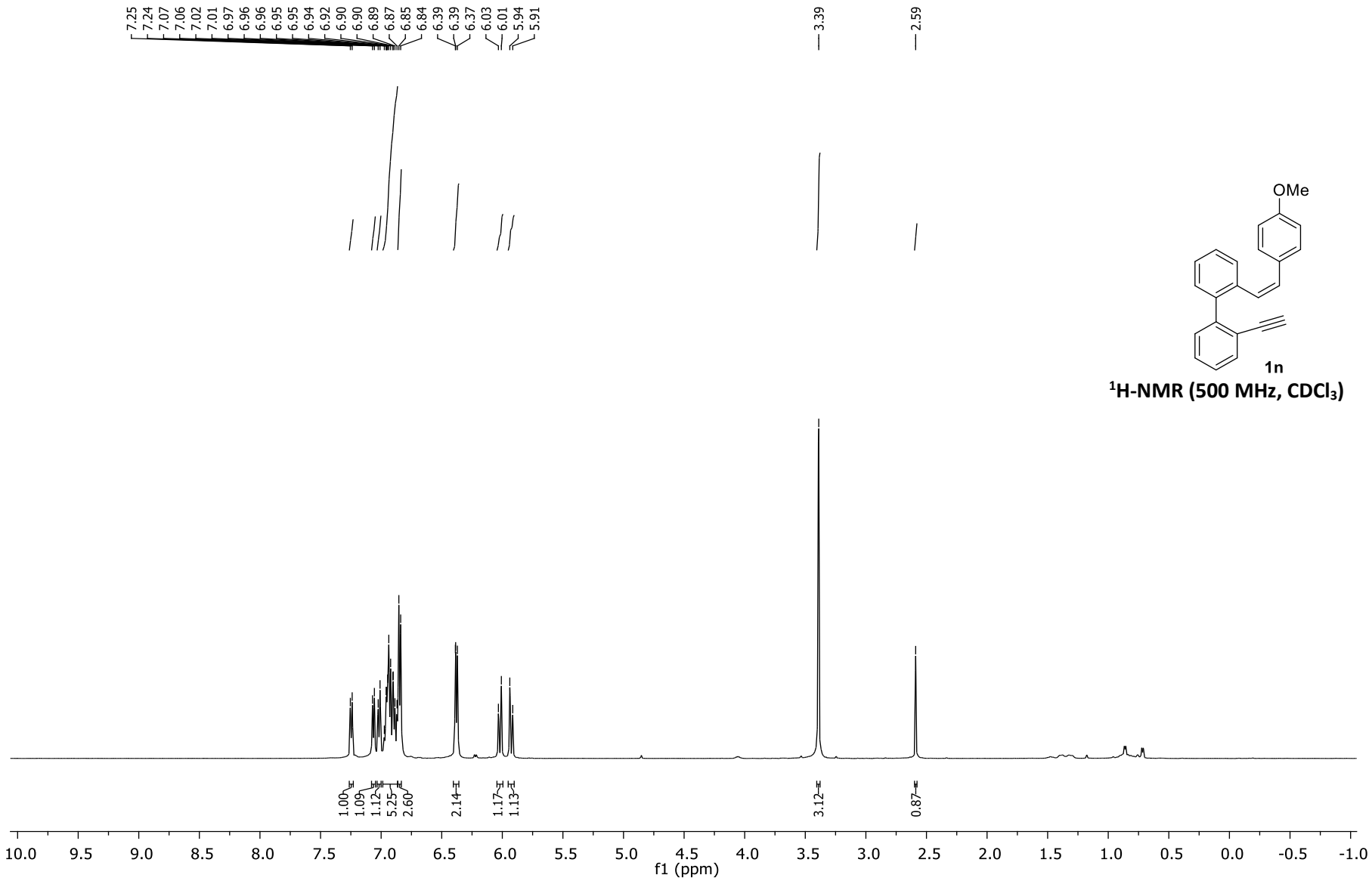


1m

^{13}C-NMR (75 MHz, $CDCl_3$)

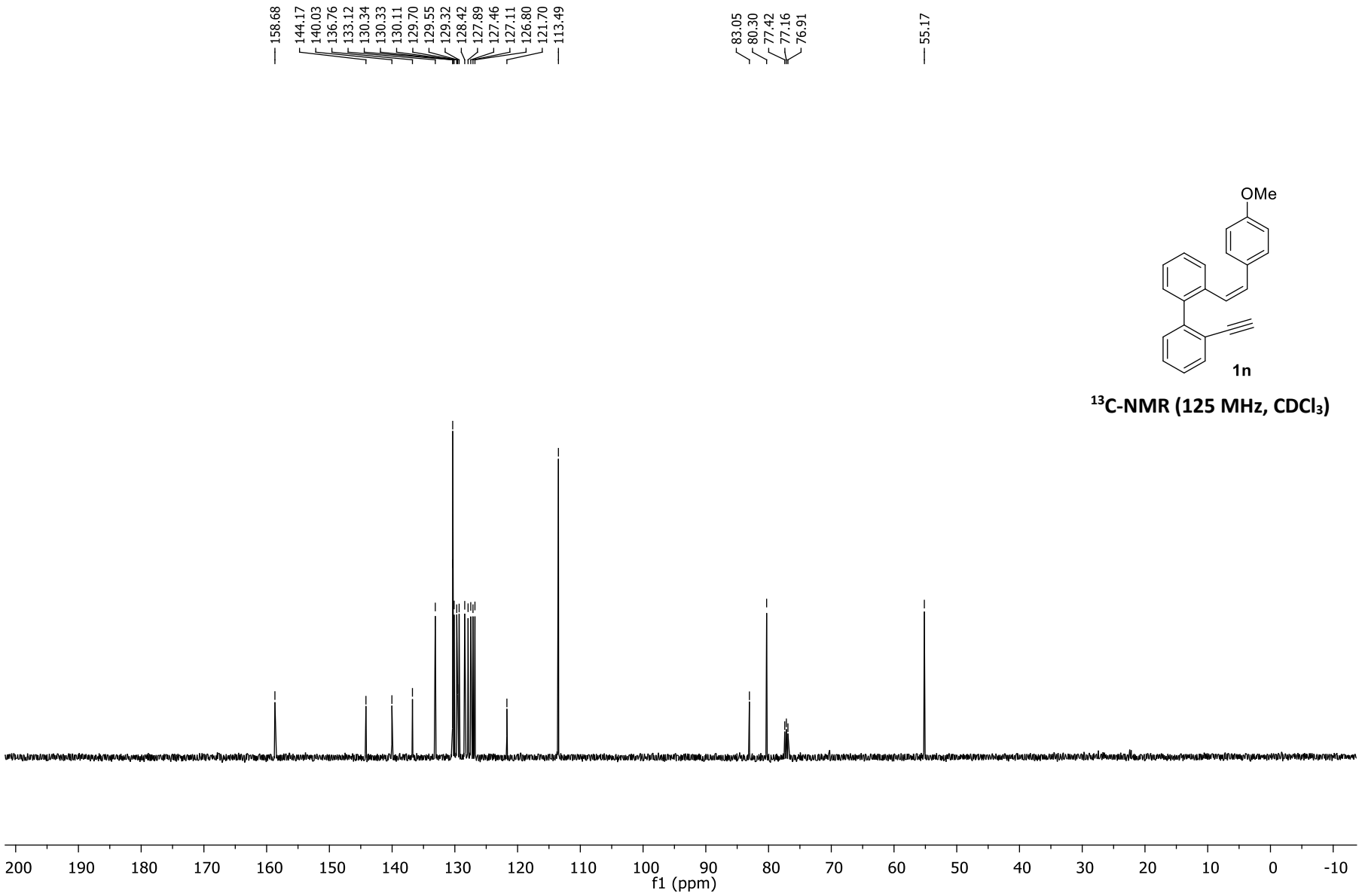

7.67
7.66
7.66
7.65
7.65
7.64
7.64
7.47
7.44
7.41
7.38
7.34
7.33
7.31
7.30
7.25
7.23
7.19
7.16
6.79
6.76
6.49
6.45
6.42
6.38
3.81
1.06
1.00
1.00
OMe
Si
TIPS-1n
1H-NMR (300 MHz, CDCl3)
1.17
1.29
1.37
4.39
0.81
2.10
2.01
1.02
0.99
2.91
18.54
3.68
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


158.63
144.12
140.26
136.59
132.95
130.60
130.32
130.22
129.81
129.57
129.35
128.33
127.91
127.35
126.98
126.77
122.71
113.54
106.20
93.86
77.58
77.16
76.74
55.18
18.67
11.35
OMe
Si
TIPS-1n
13C-NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

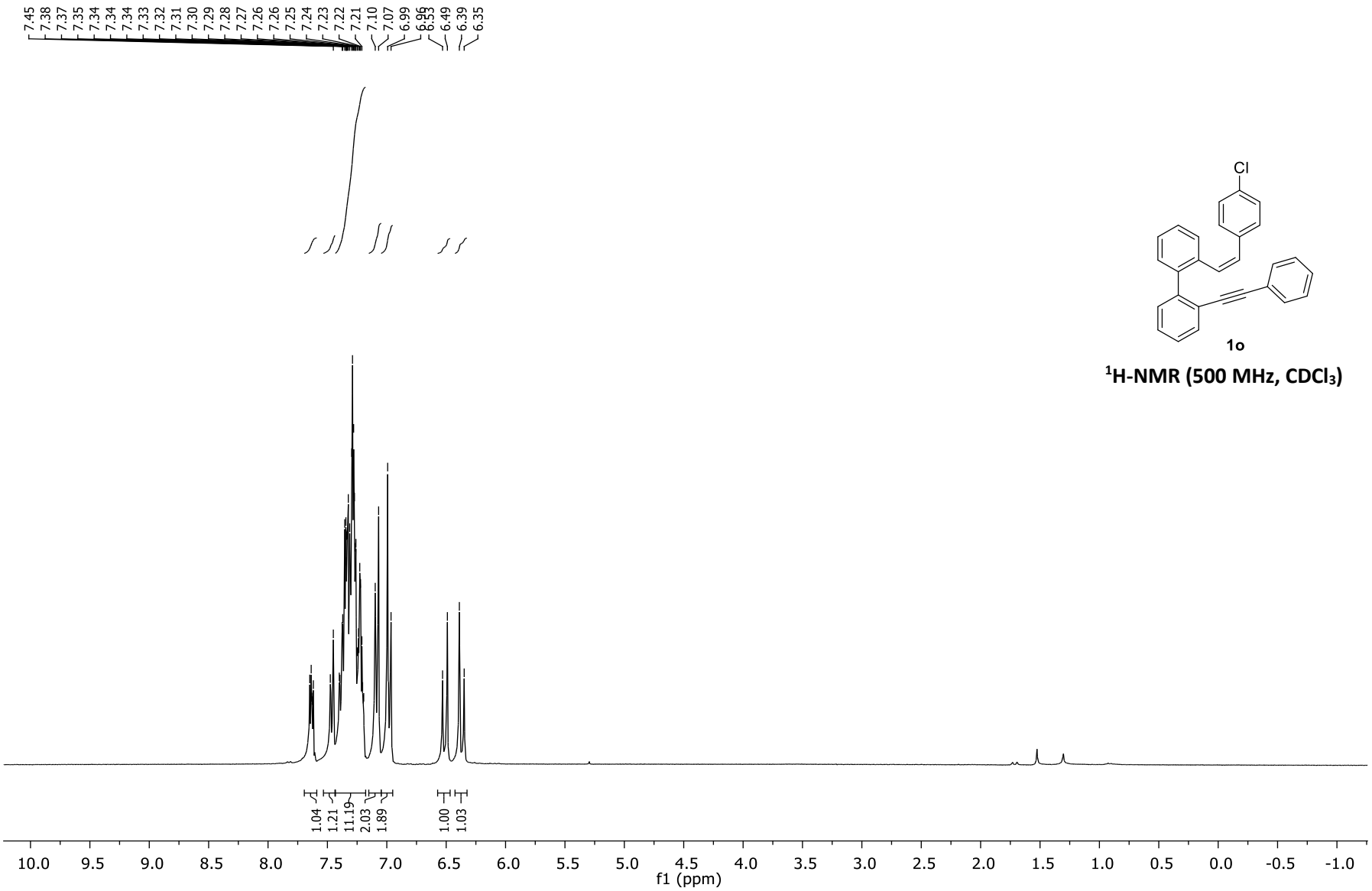


1n

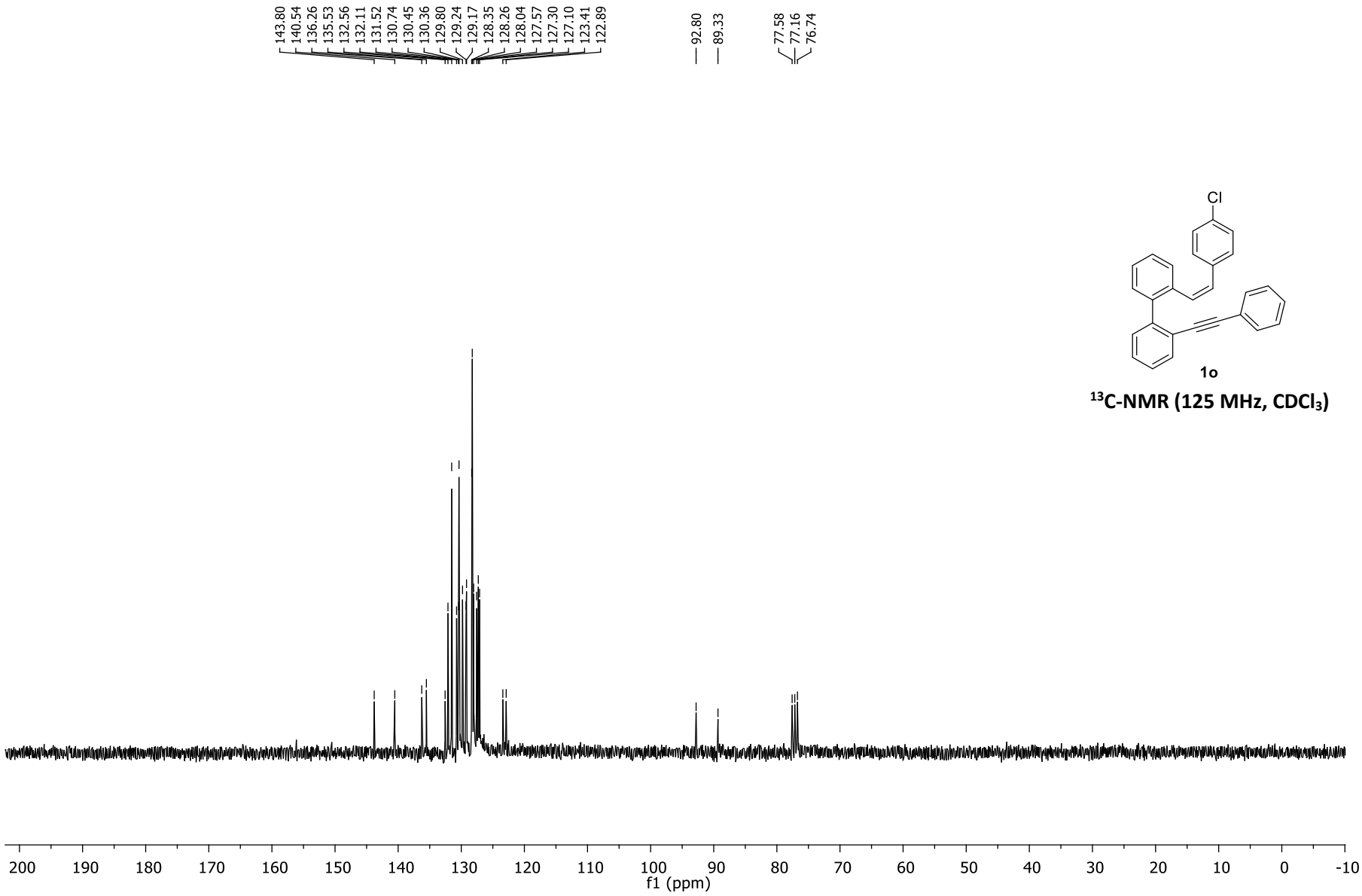
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

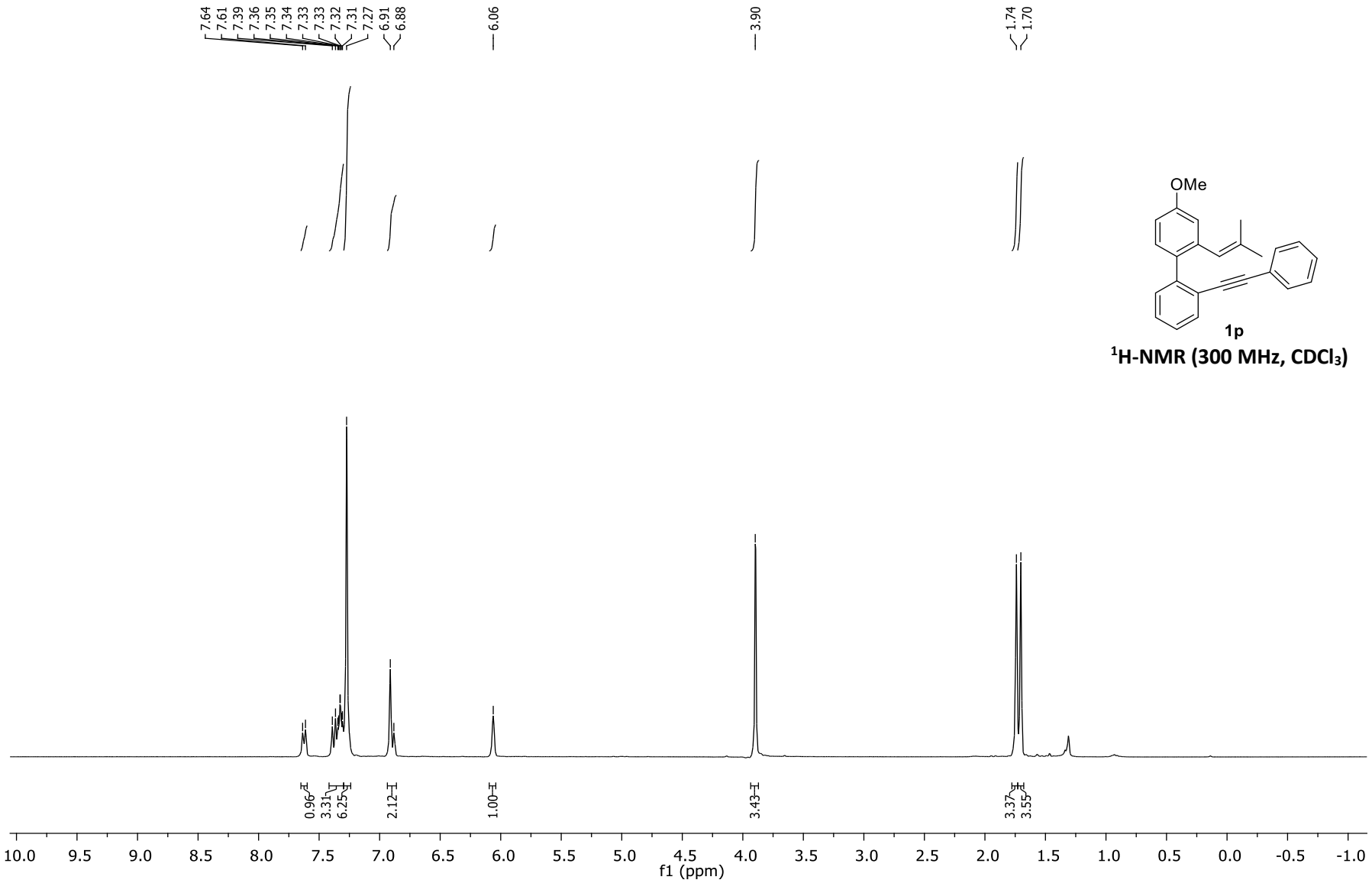


^{1}H-NMR (500 MHz, $CDCl_3$)



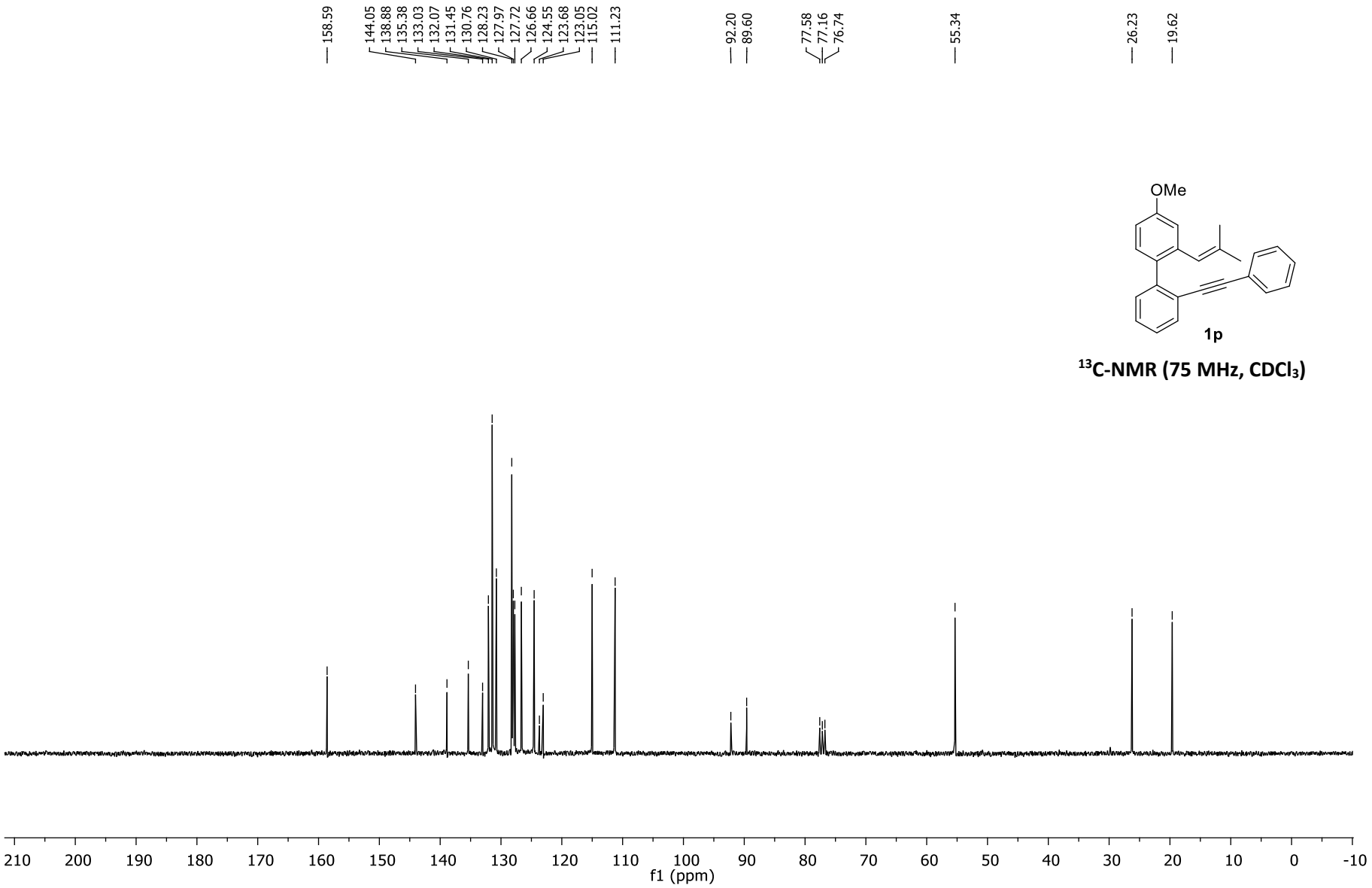
1o

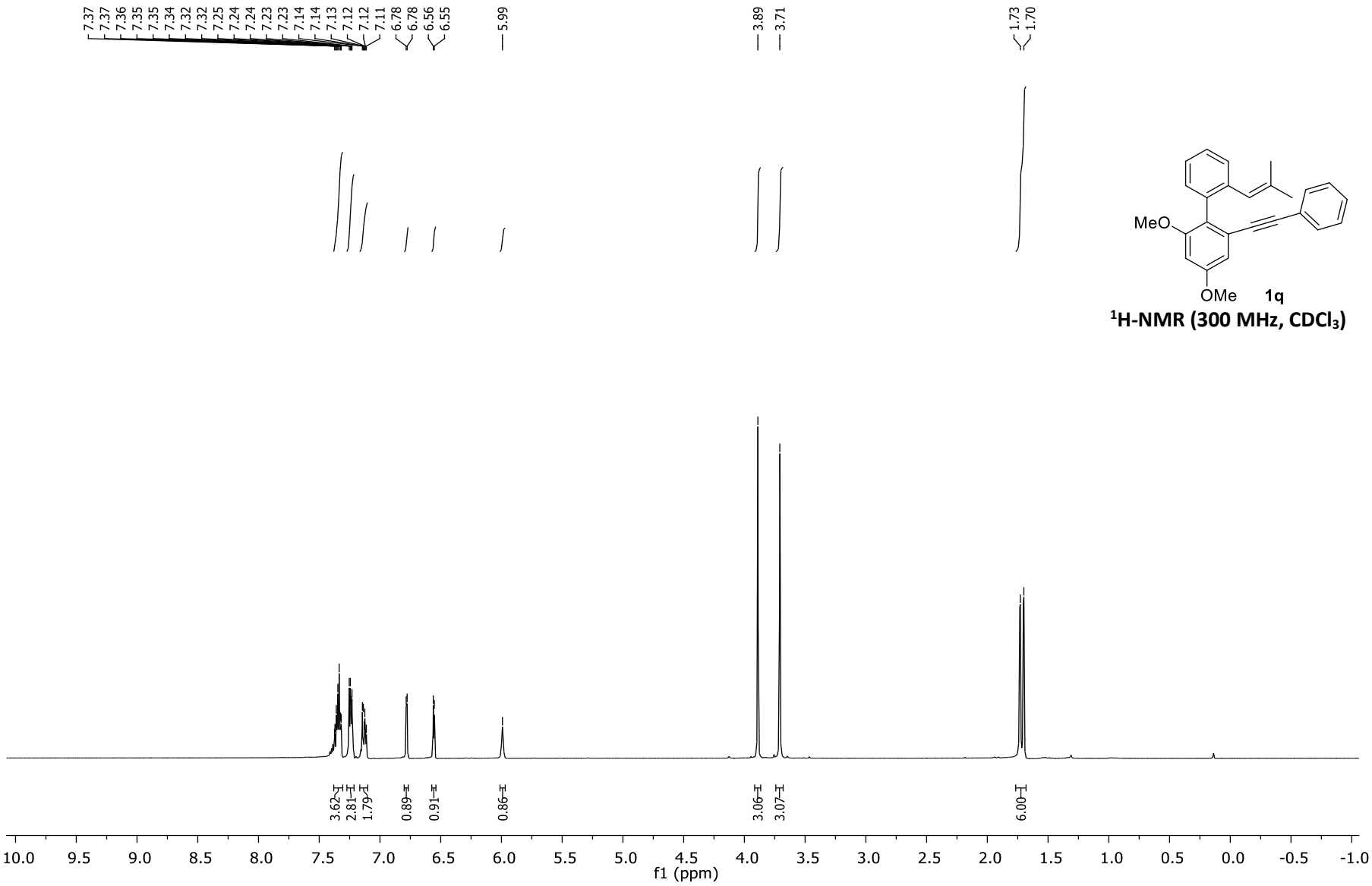
^{13}C-NMR (125 MHz, $CDCl_3$)



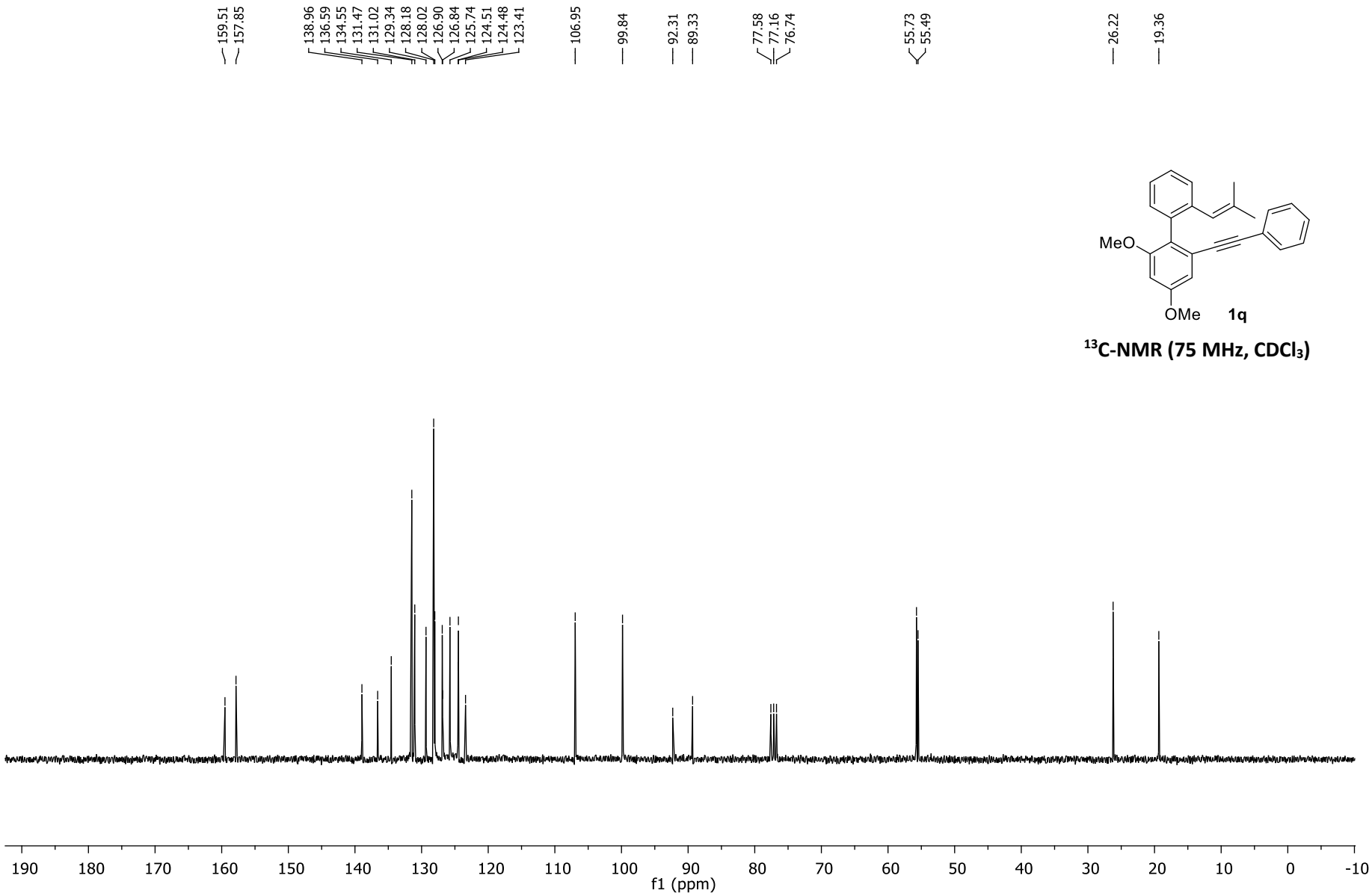
1p

^{1}H-NMR (300 MHz, $CDCl_3$)

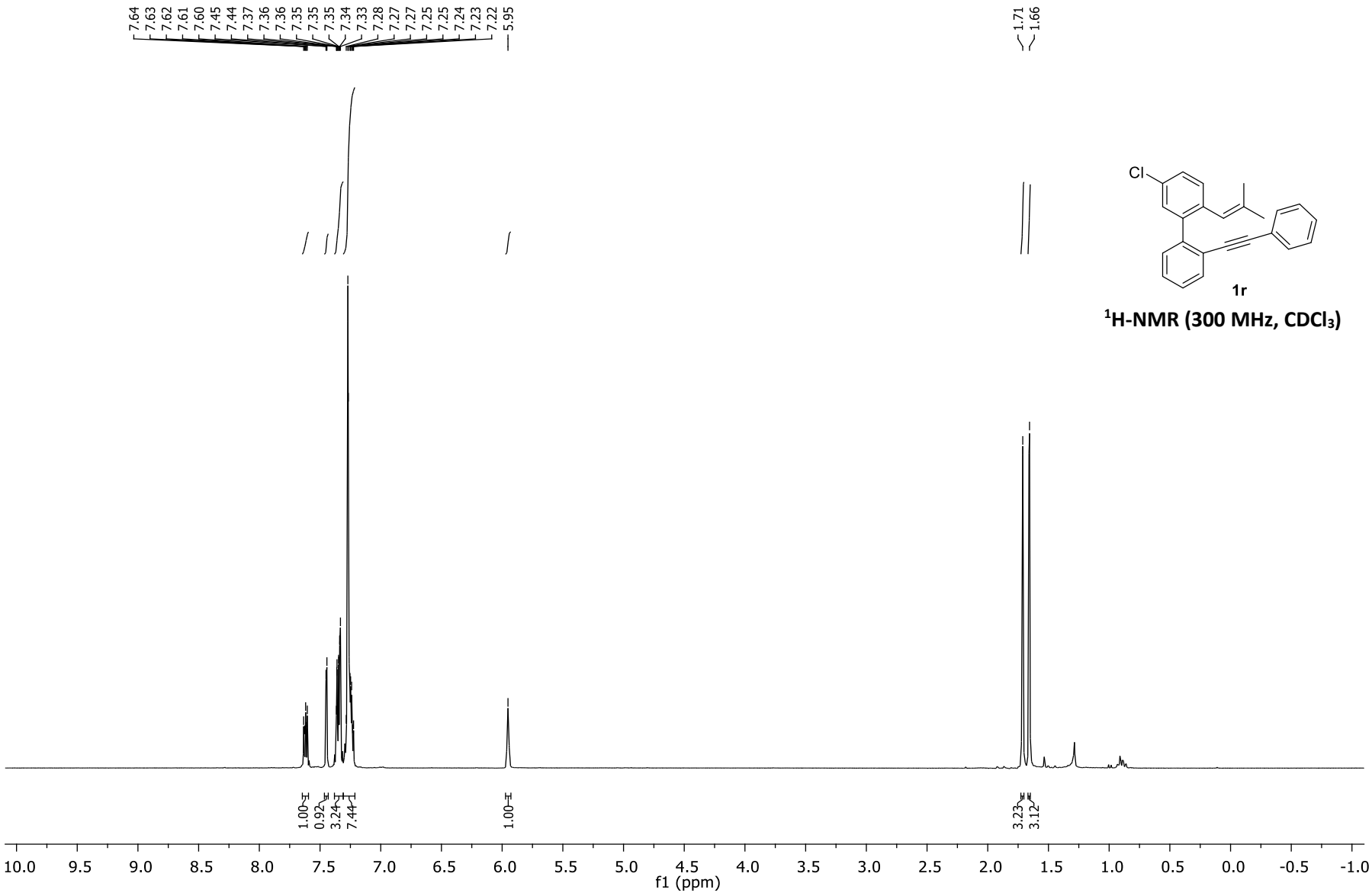

158.59
144.05
138.88
135.38
133.03
132.07
131.45
130.76
128.23
127.97
127.72
126.66
124.55
123.68
123.05
115.02
111.23
92.20
89.60
77.58
77.16
76.74
55.34
26.23
19.62
OMe
1p
^{13}C-NMR (75 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



^{1}H-NMR (300 MHz, $CDCl_3$)

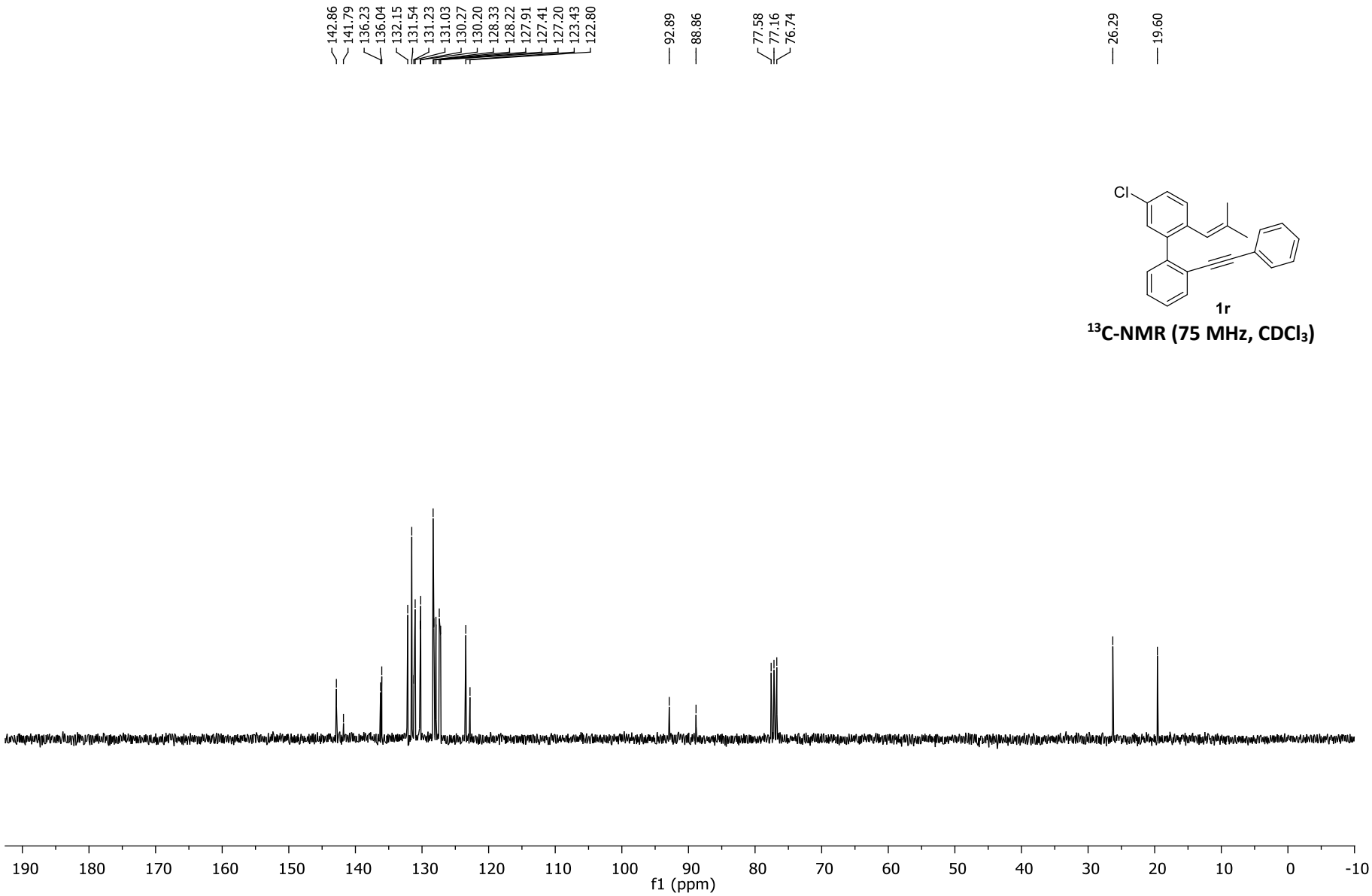


^{13}C-NMR (75 MHz, $CDCl_3$)

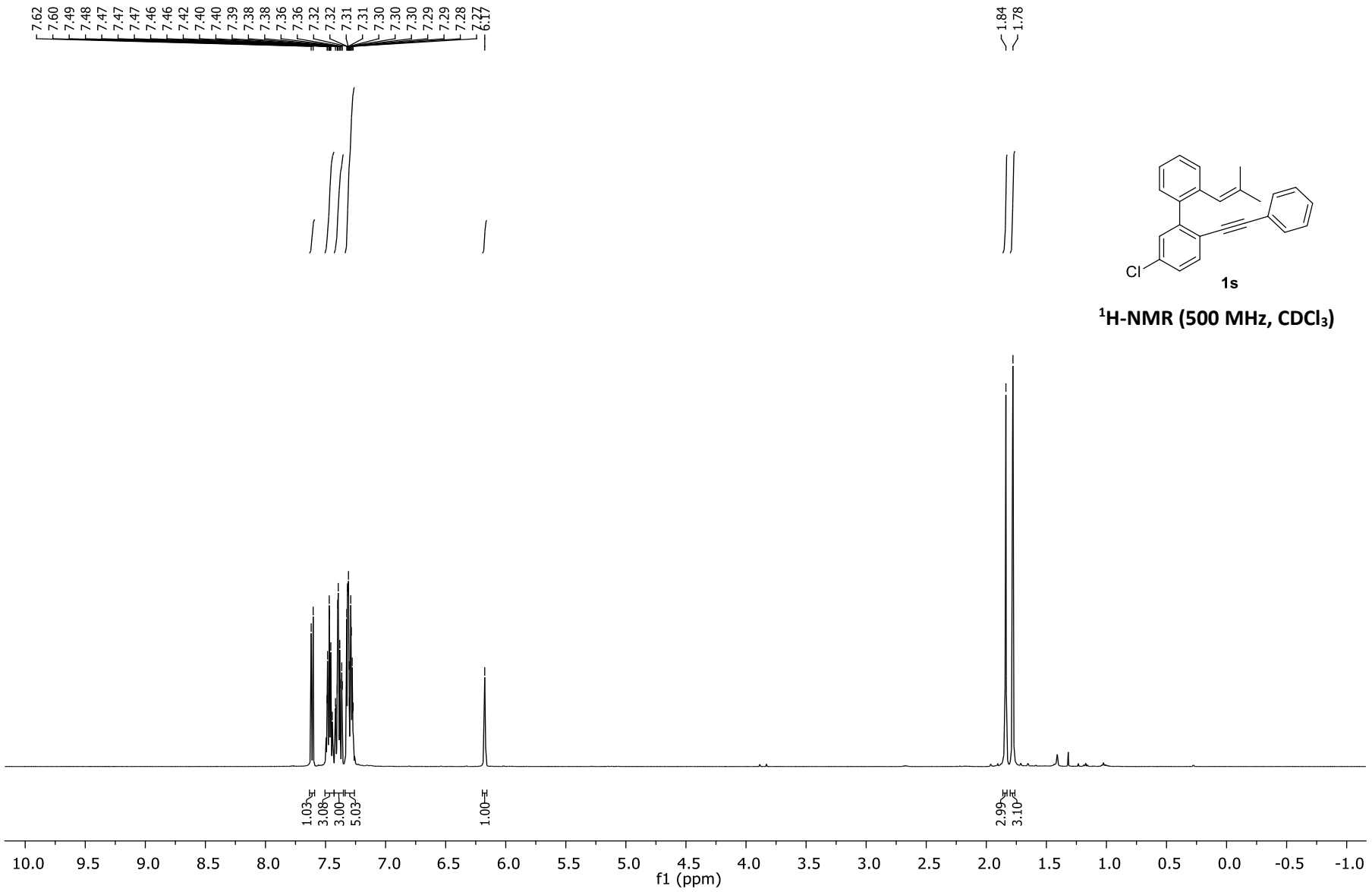


1r

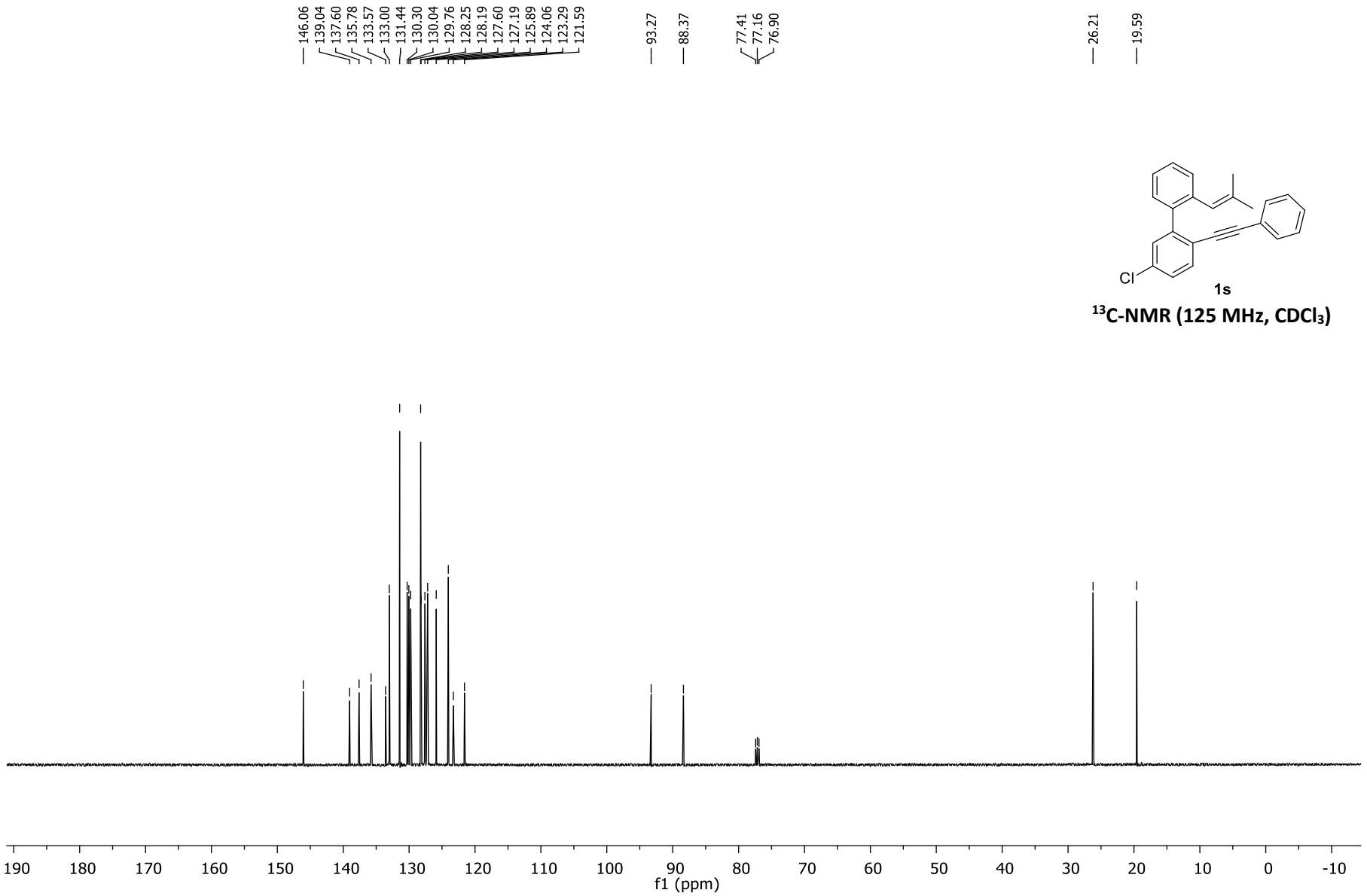
^{1}H-NMR (300 MHz, $CDCl_3$)



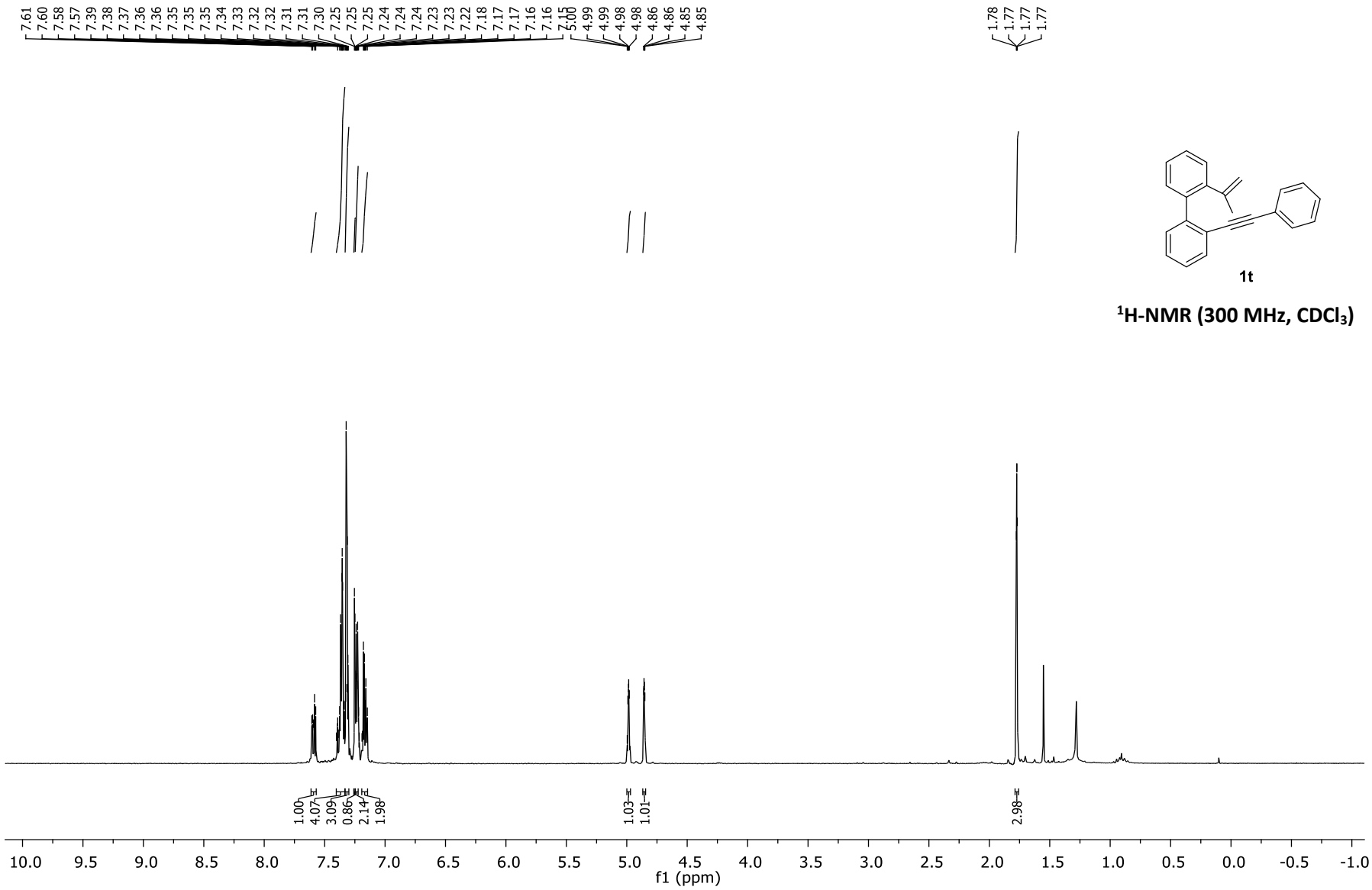
^{13}C-NMR (75 MHz, $CDCl_3$)



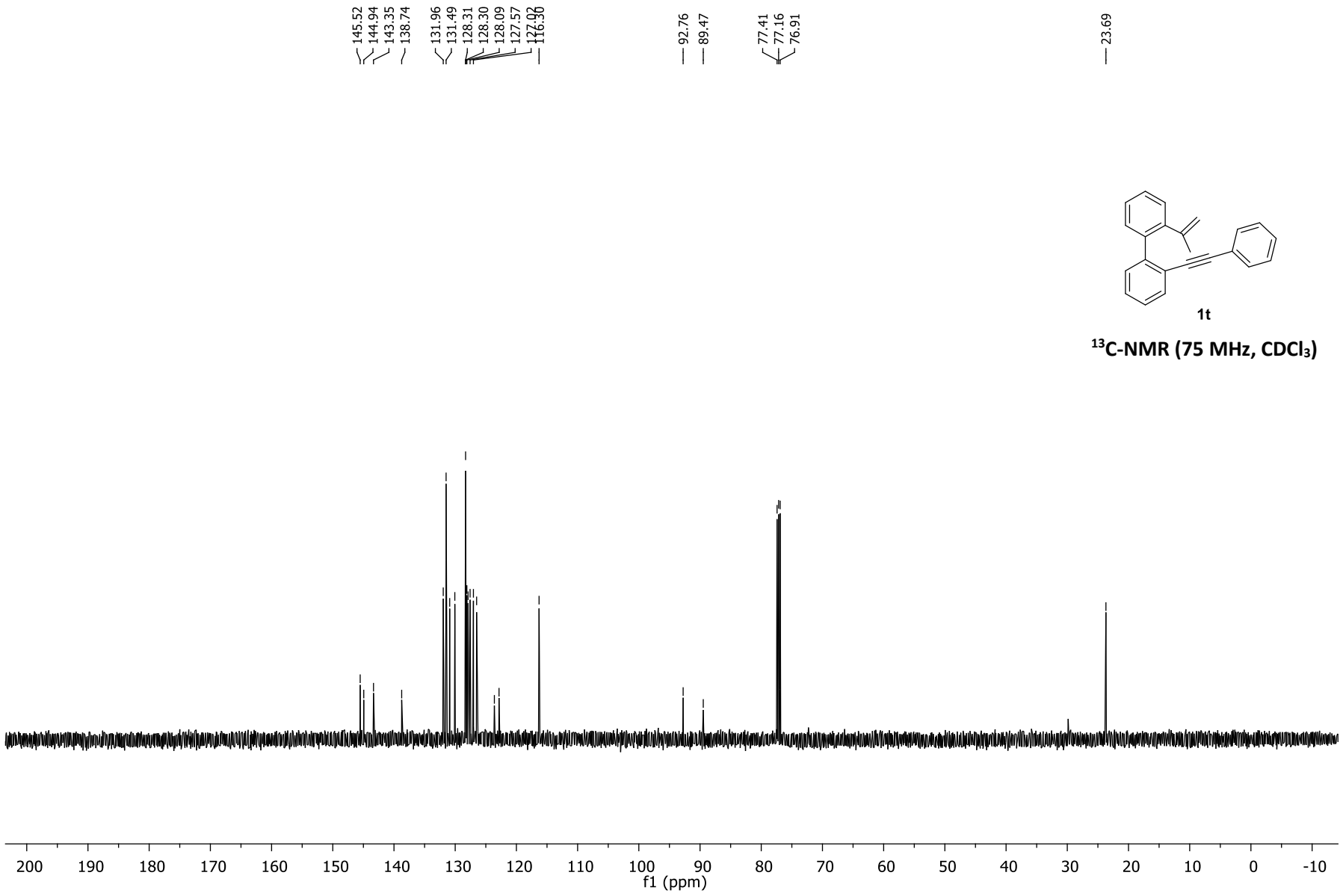
^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

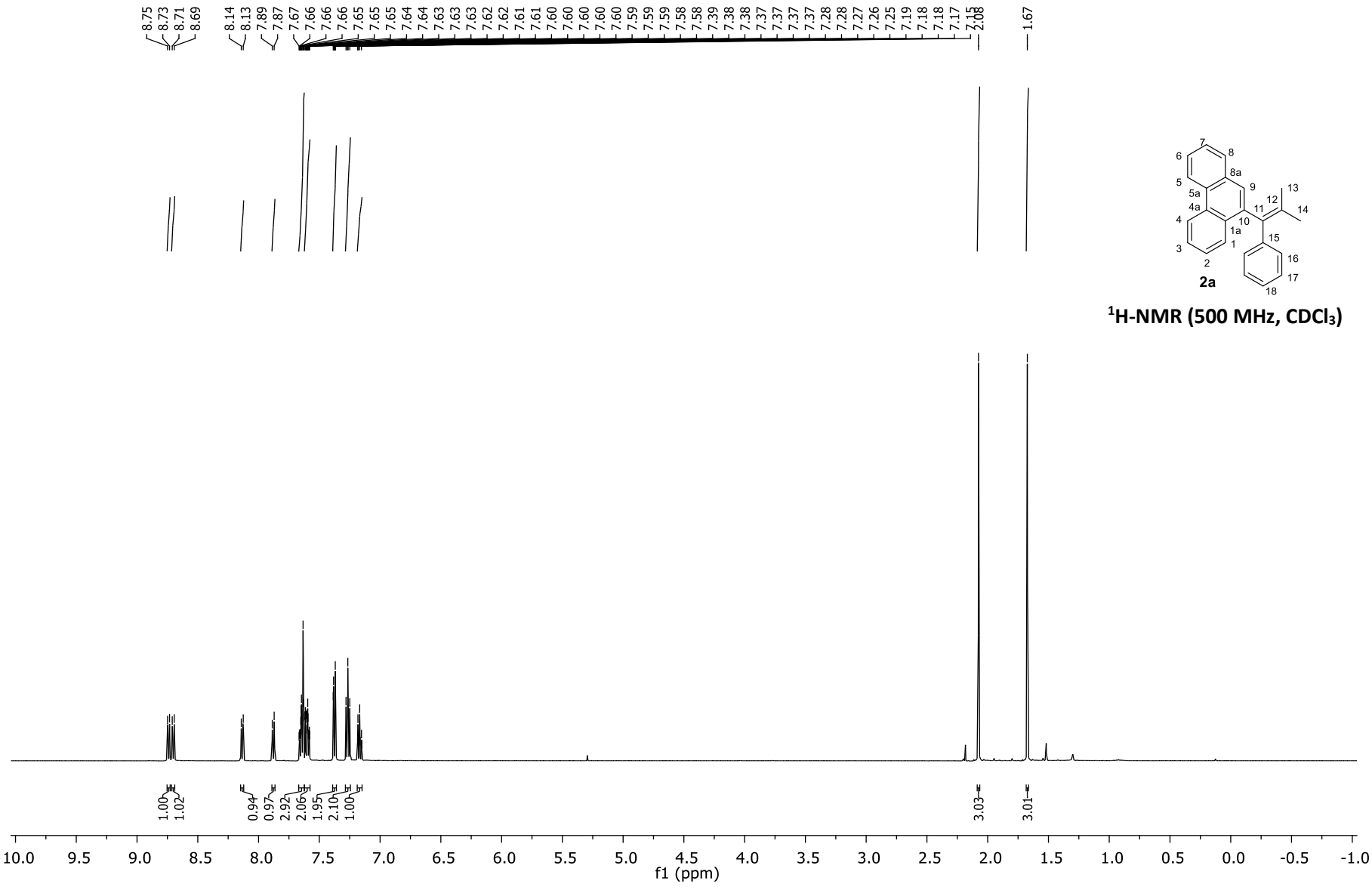


^{1}H-NMR (300 MHz, $CDCl_3$)



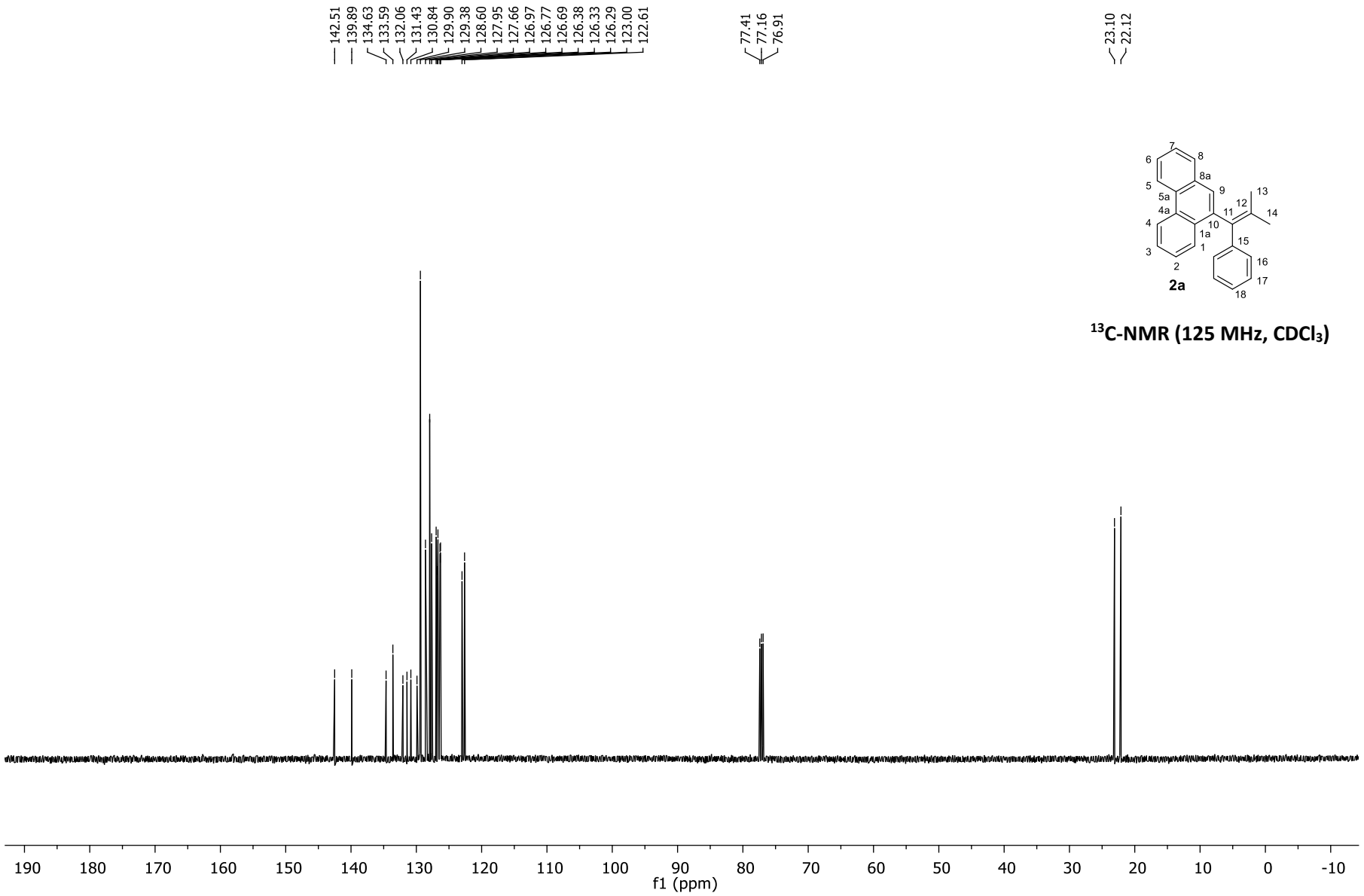
1t

^{13}C-NMR (75 MHz, $CDCl_3$)

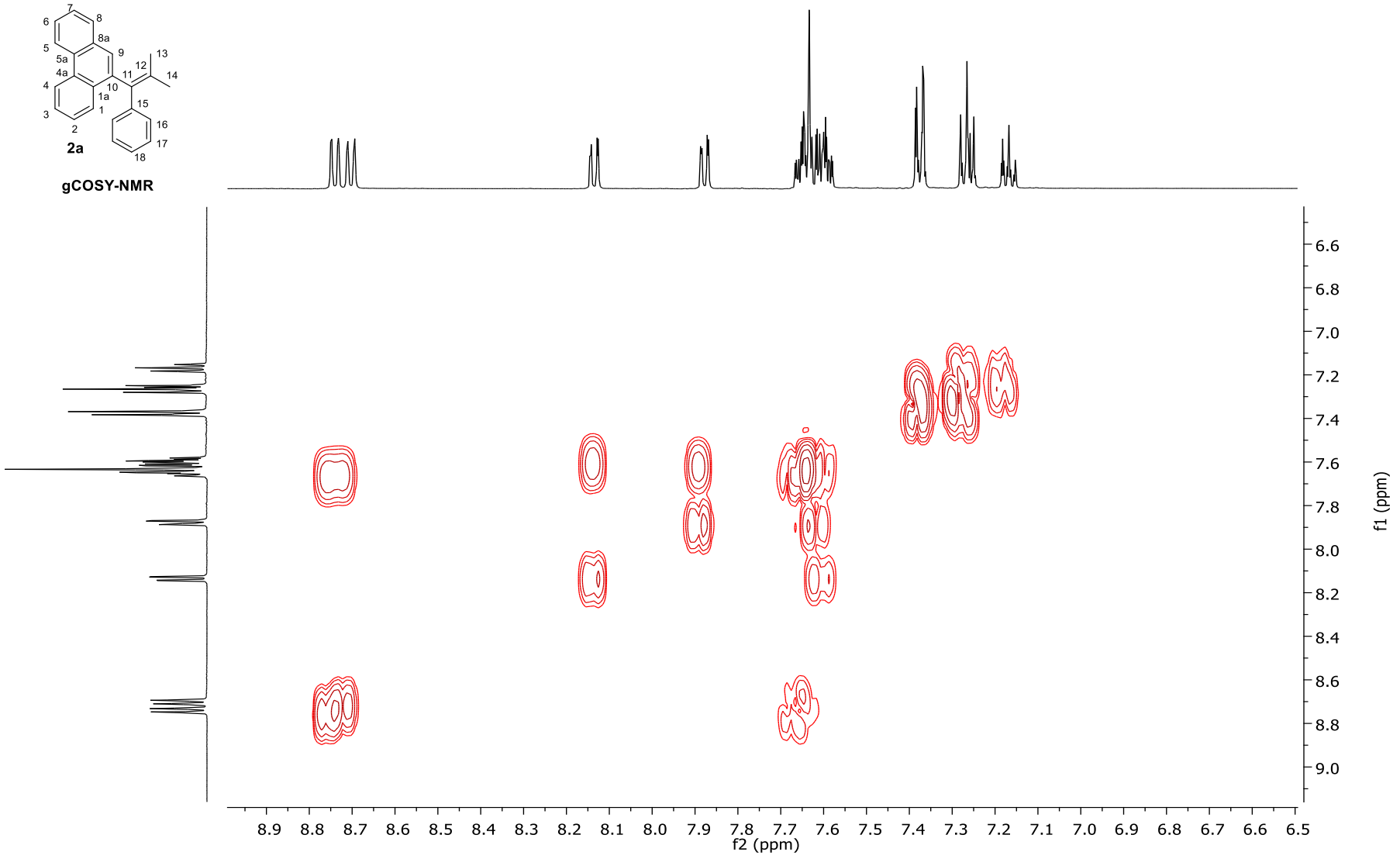


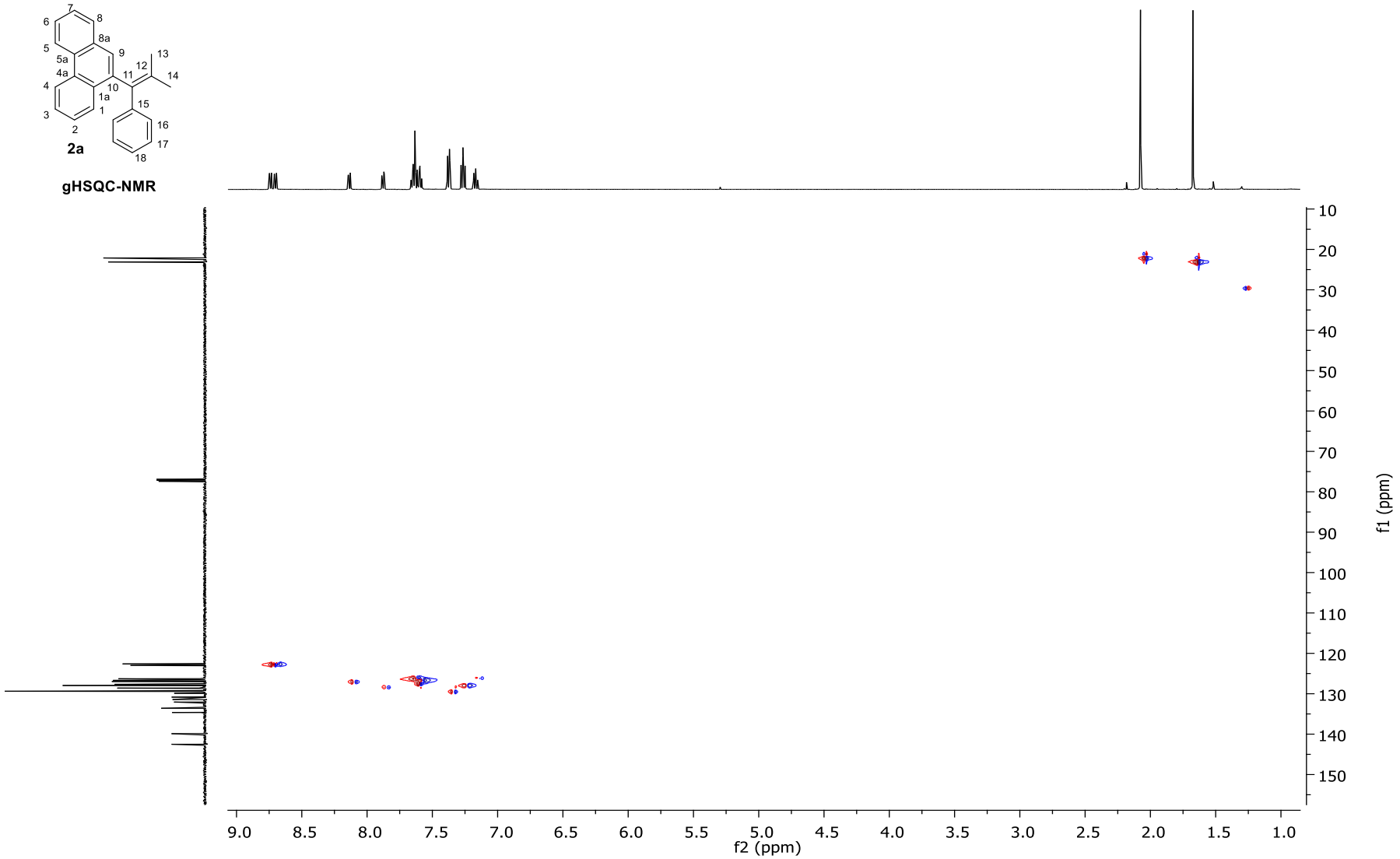
2a

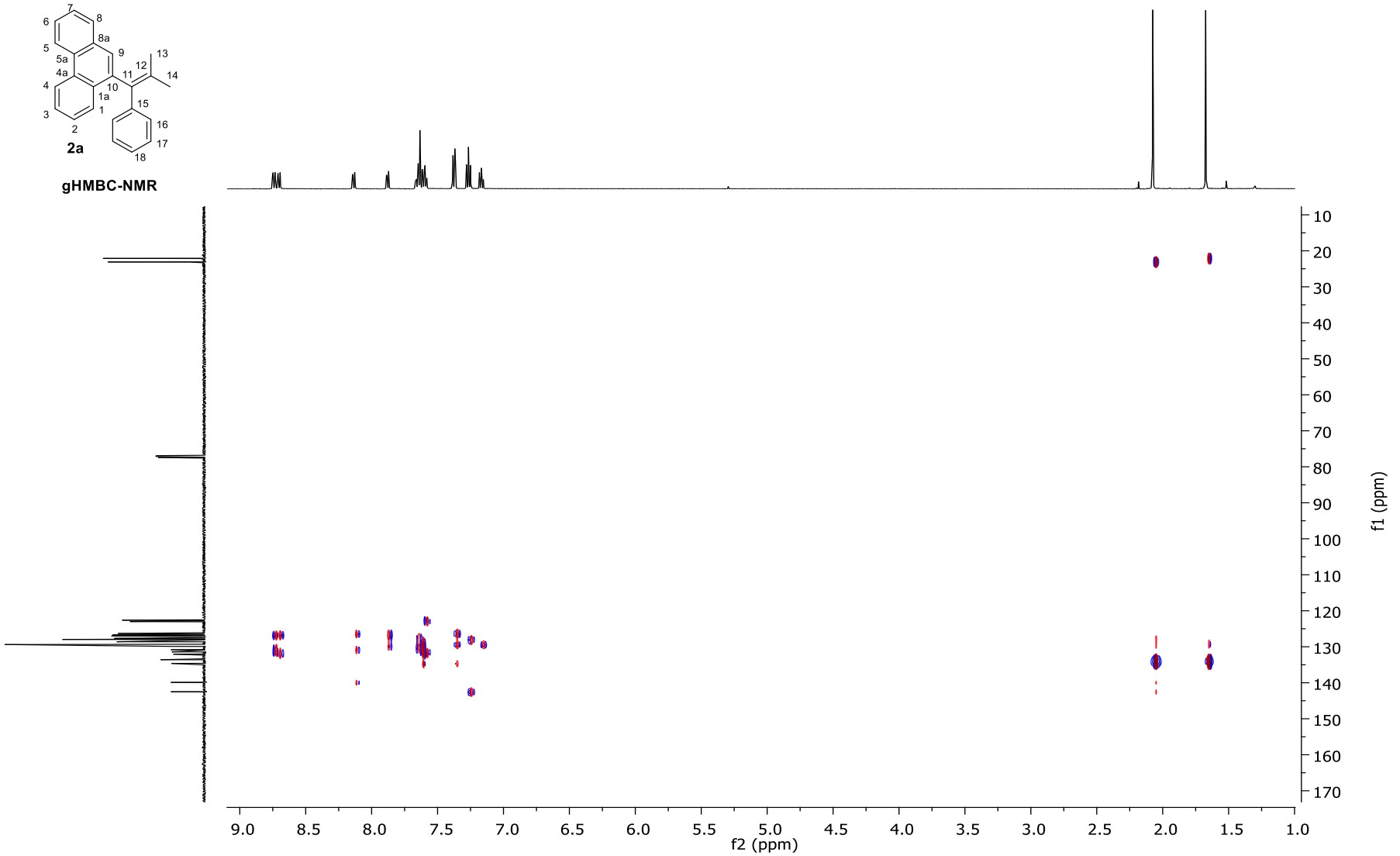
^{1}H-NMR (500 MHz, $CDCl_3$)

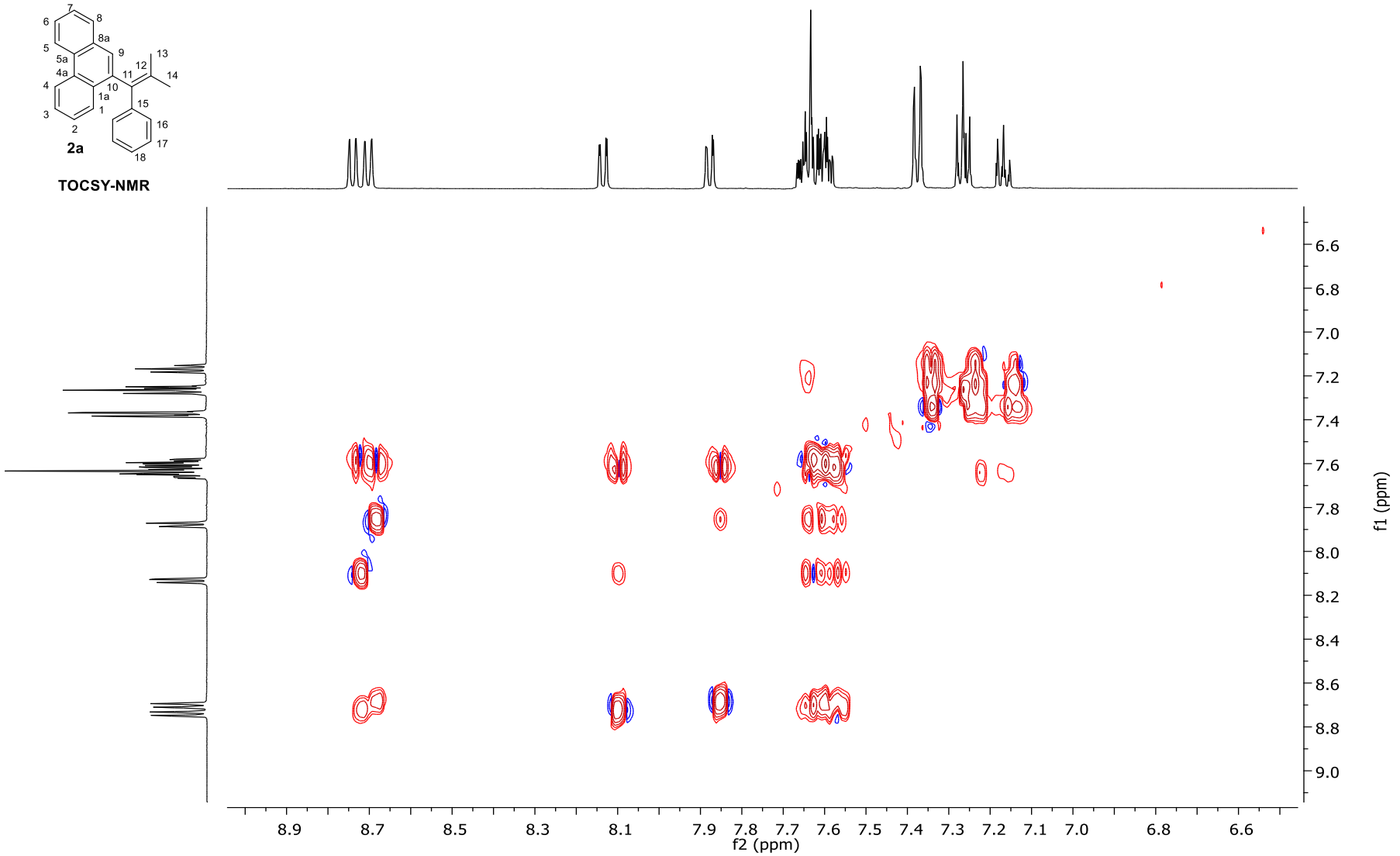


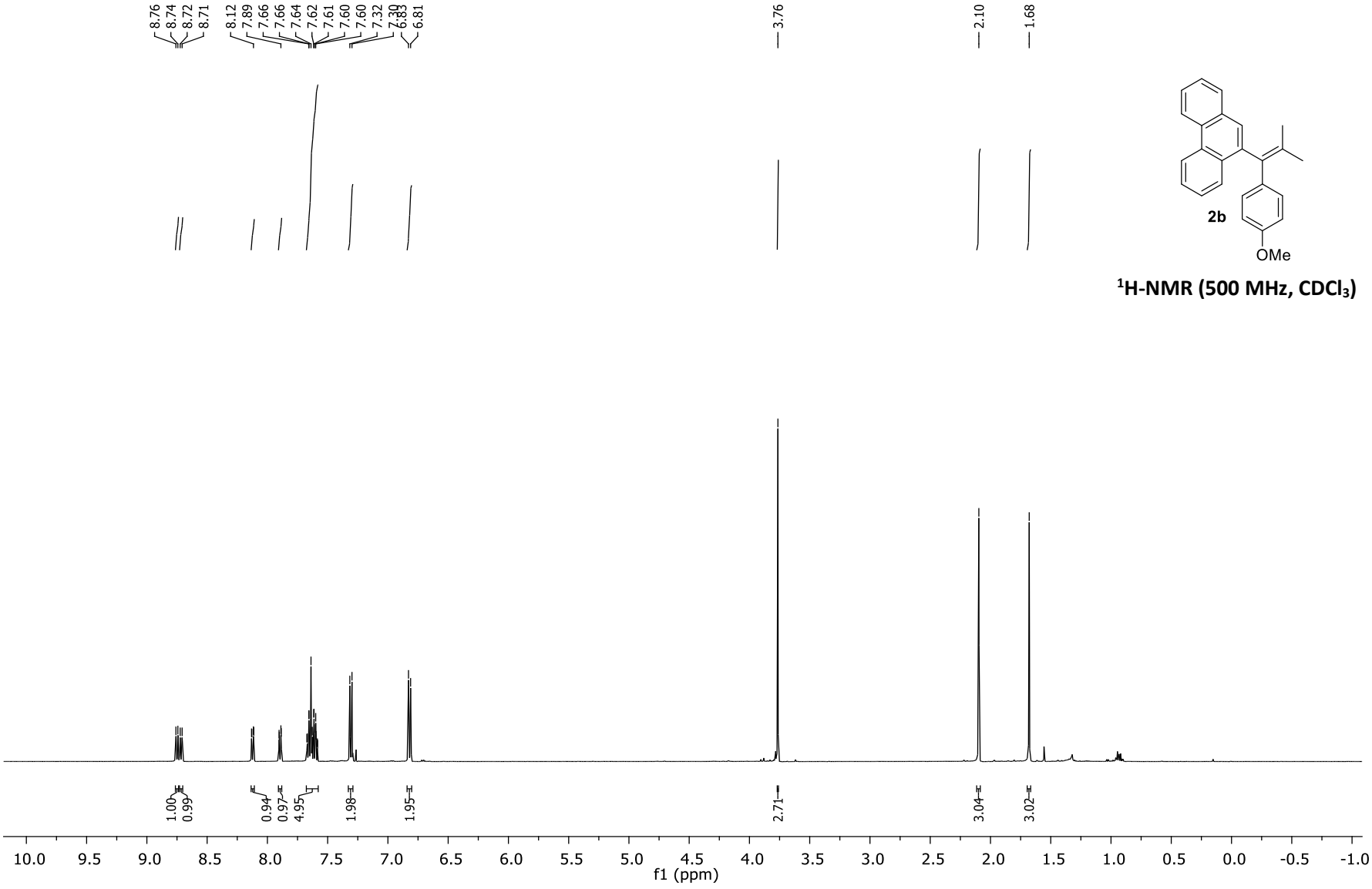
^{13}C-NMR (125 MHz, $CDCl_3$)


2a
gCOSY-NMR
f2 (ppm)
f1 (ppm)

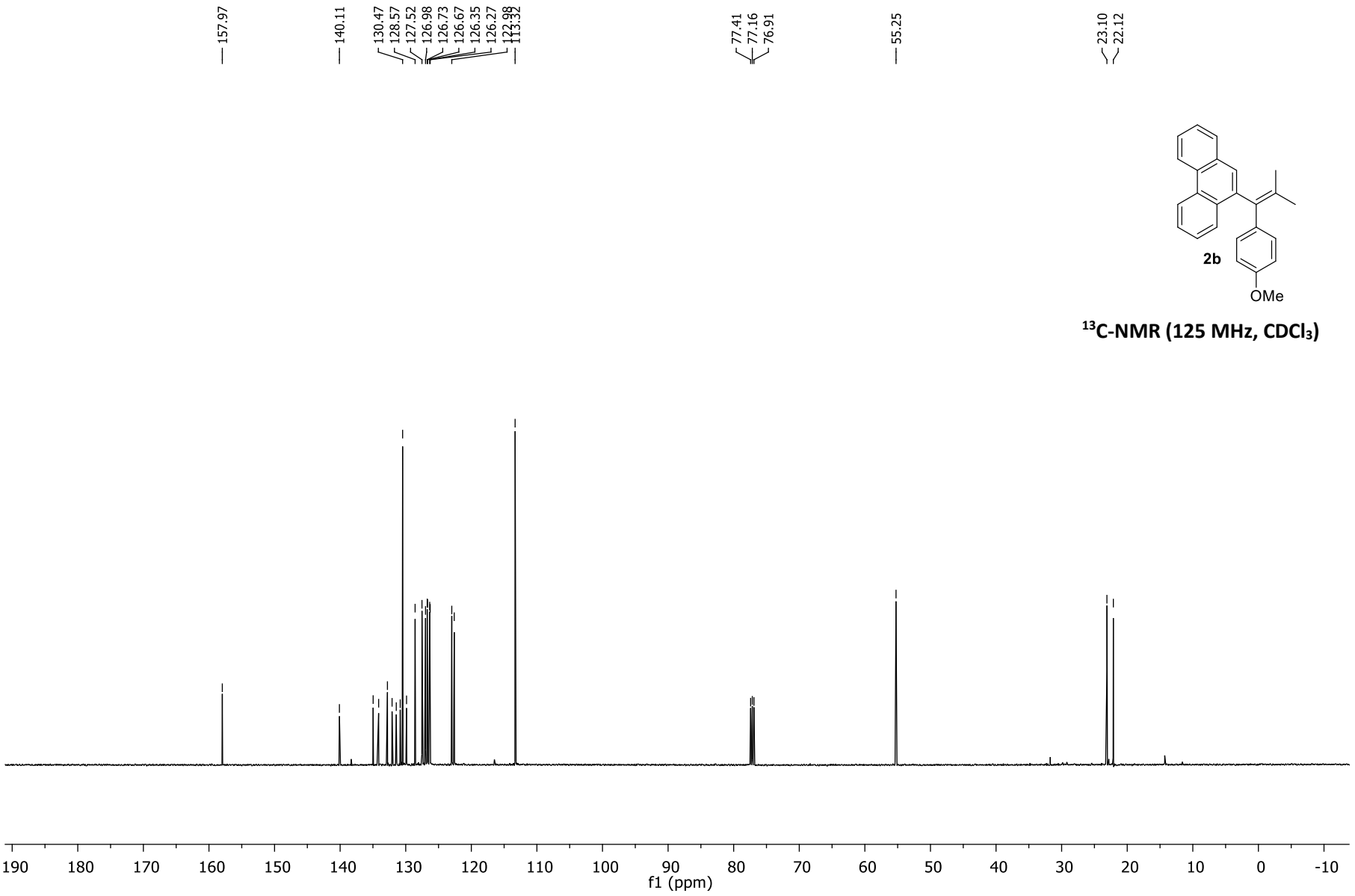

2a
gHSQC-NMR
f2 (ppm)
f1 (ppm)


2a
gHMBC-NMR
f2 (ppm)
f1 (ppm)

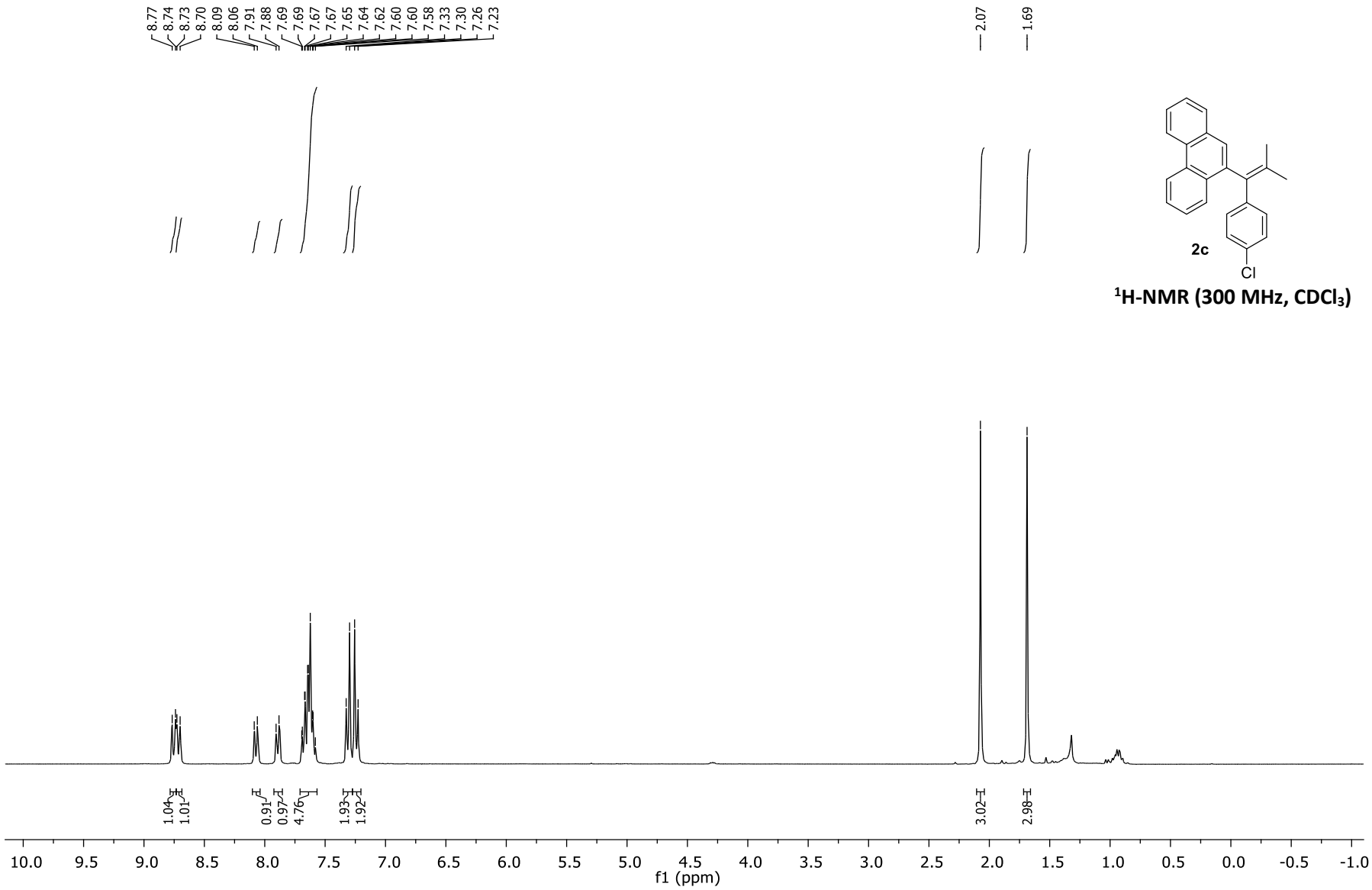

2a
TOCSY-NMR
f2 (ppm)
f1 (ppm)



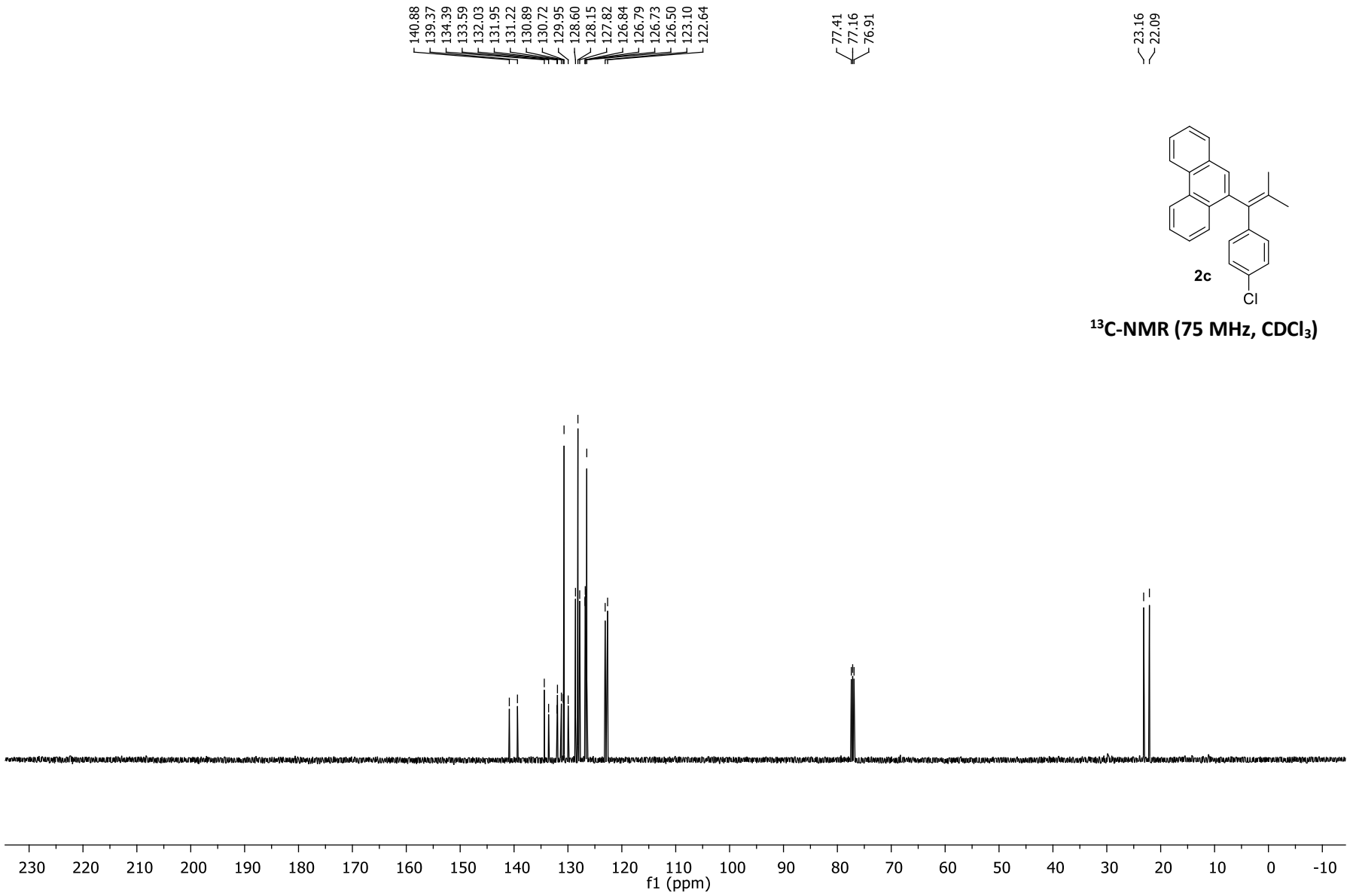
^{1}H-NMR (500 MHz, $CDCl_3$)



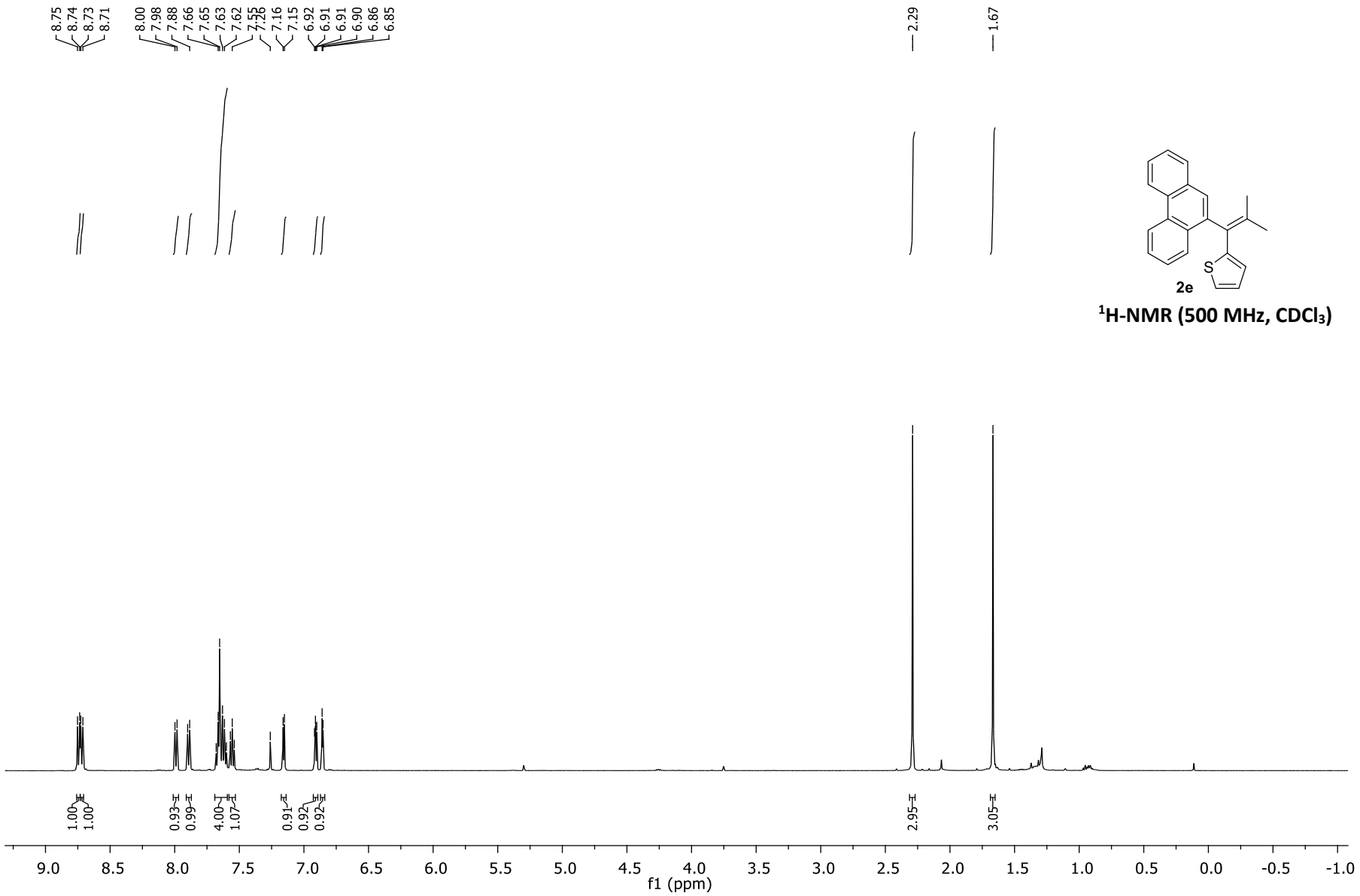
^{13}C-NMR (125 MHz, $CDCl_3$)



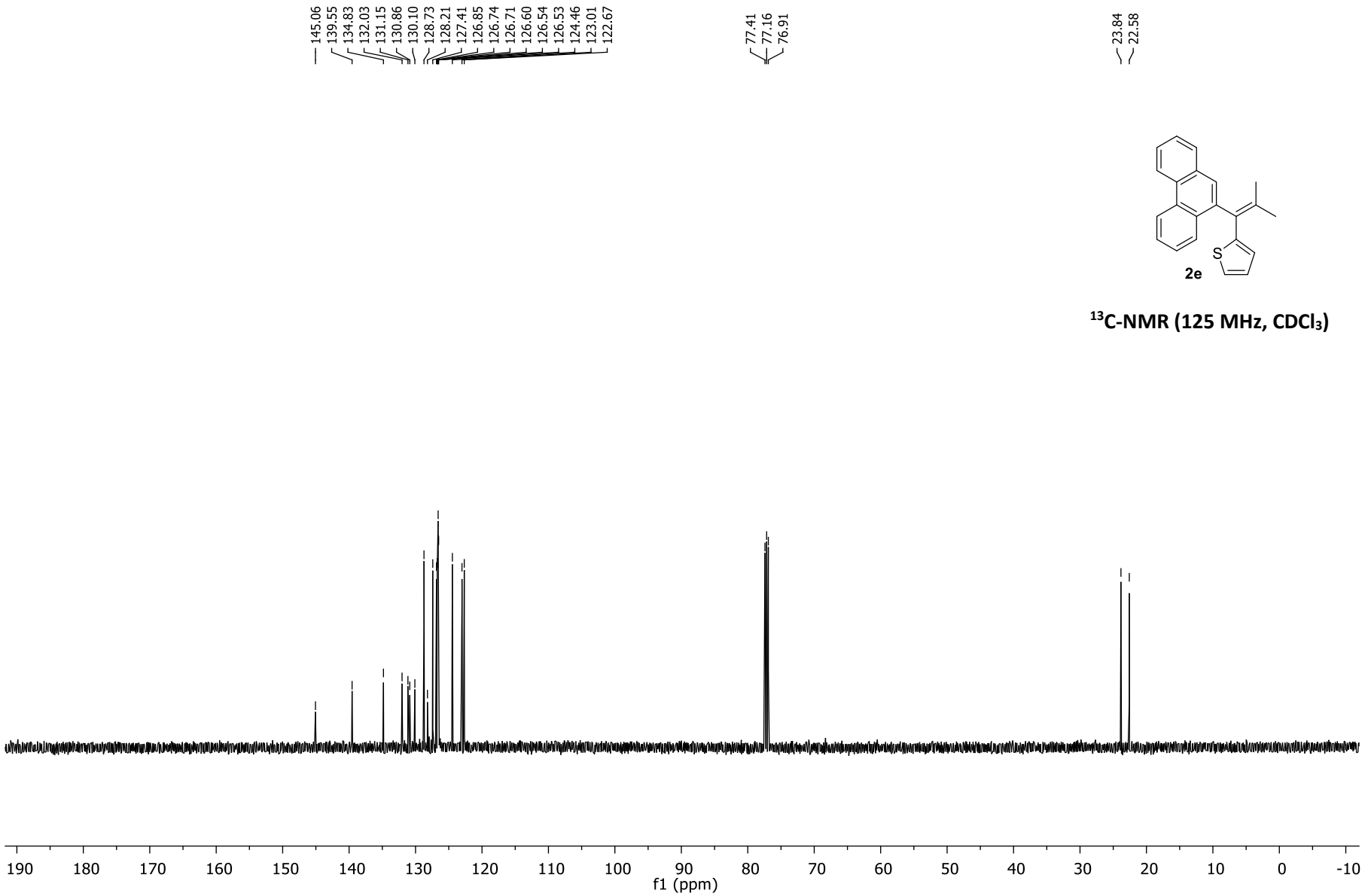
^{1}H-NMR (300 MHz, $CDCl_3$)



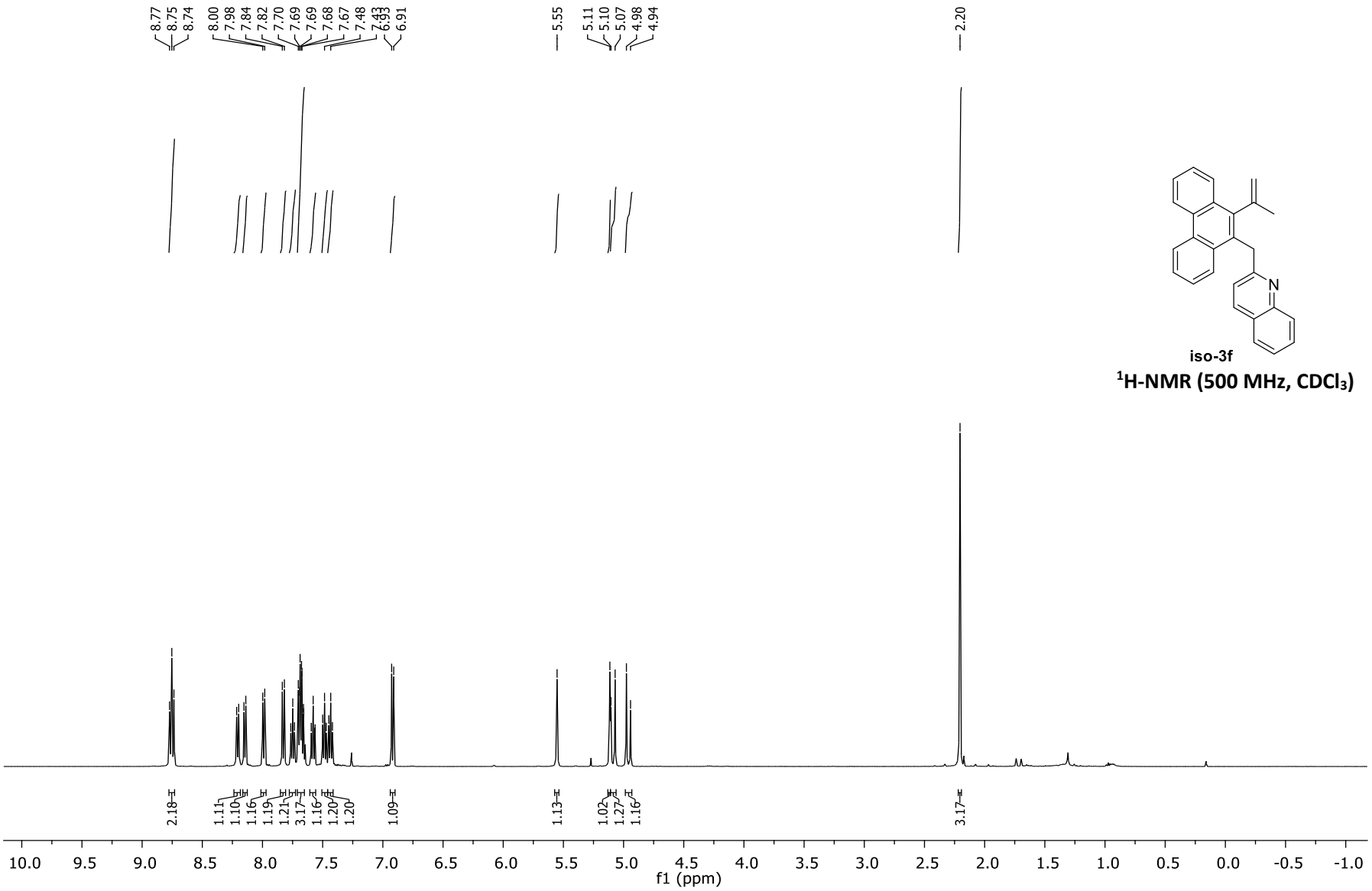
^{13}C-NMR (75 MHz, $CDCl_3$)



^{1}H-NMR (500 MHz, $CDCl_3$)

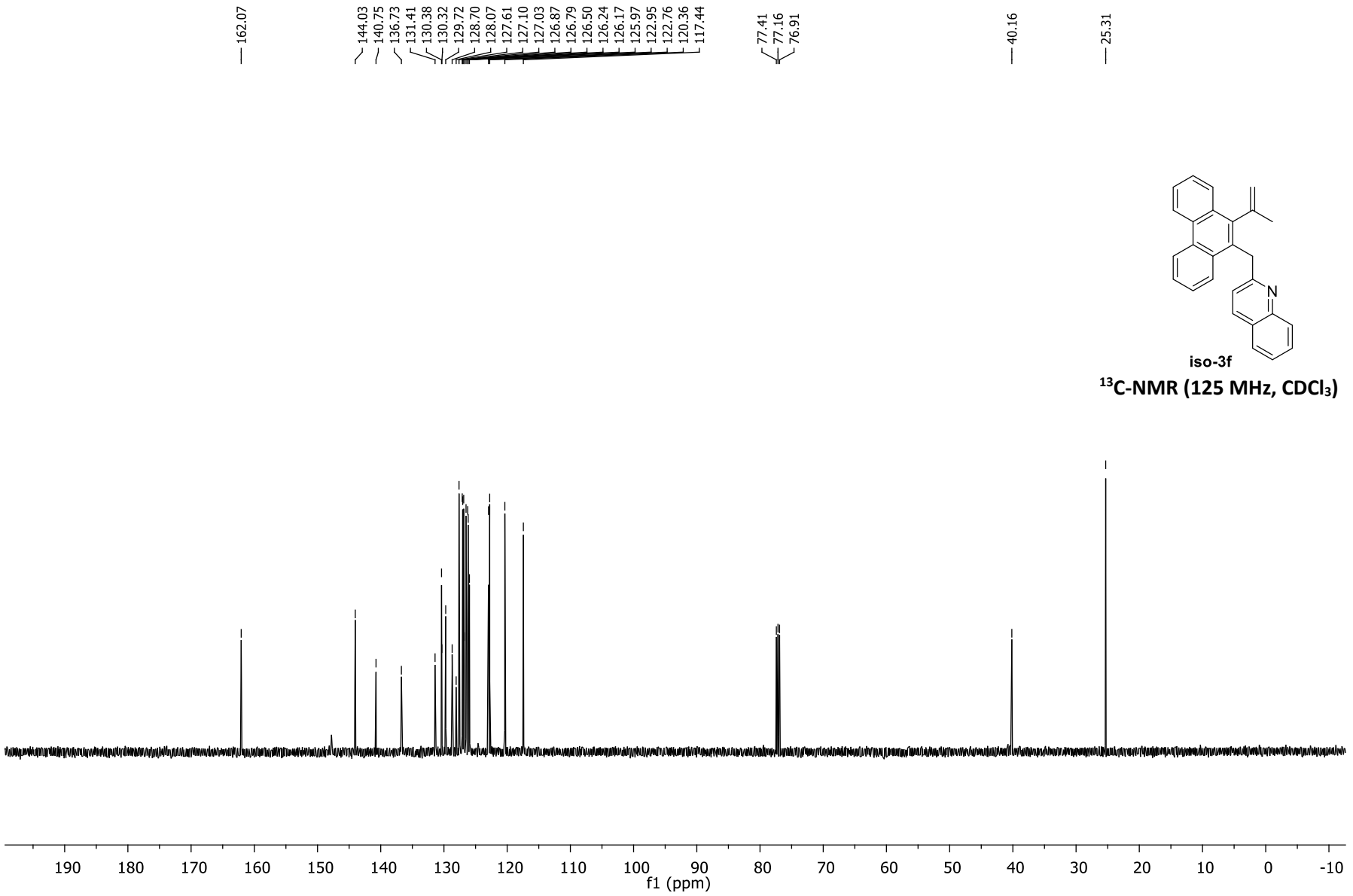


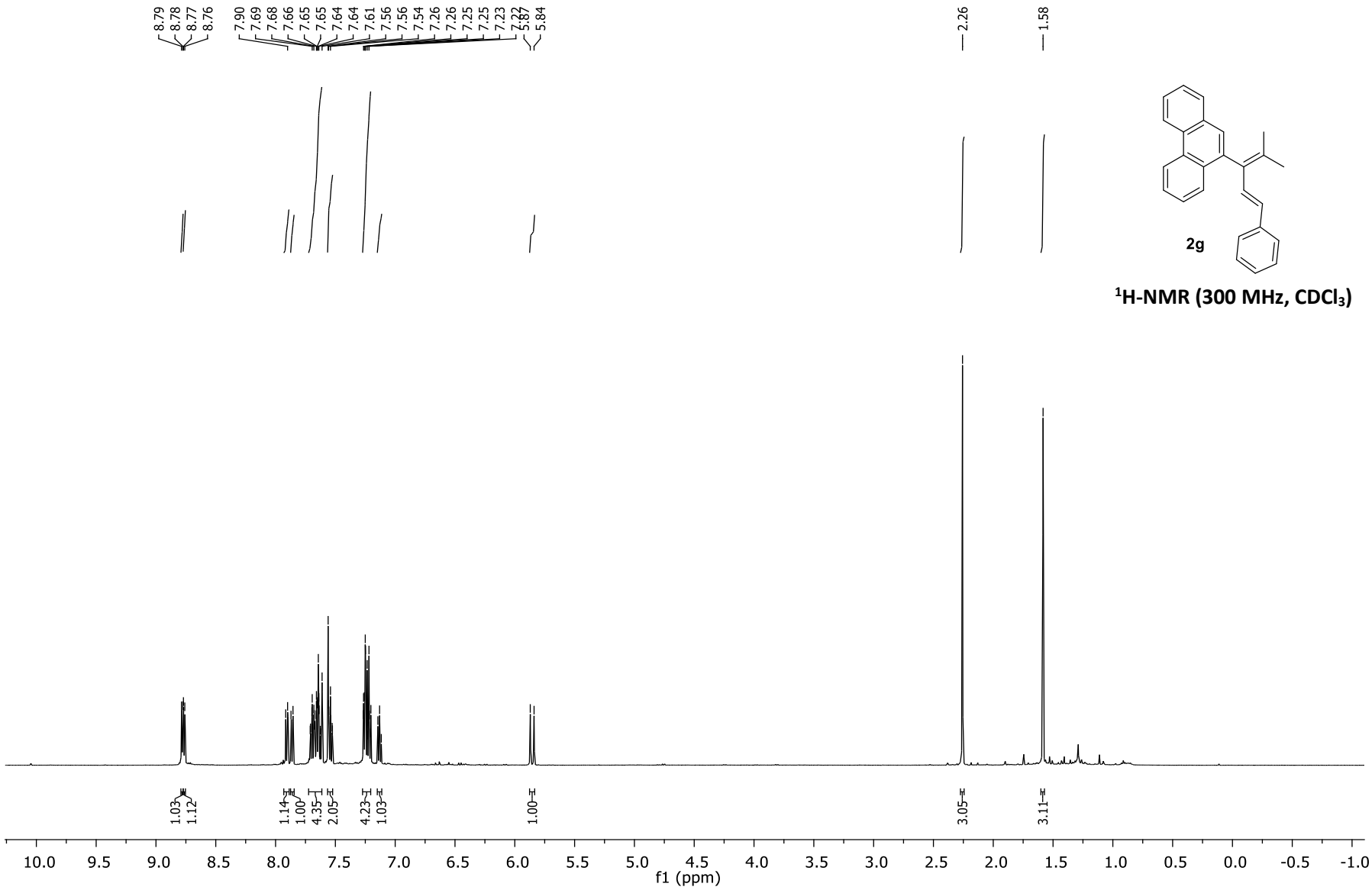
^{13}C-NMR (125 MHz, $CDCl_3$)



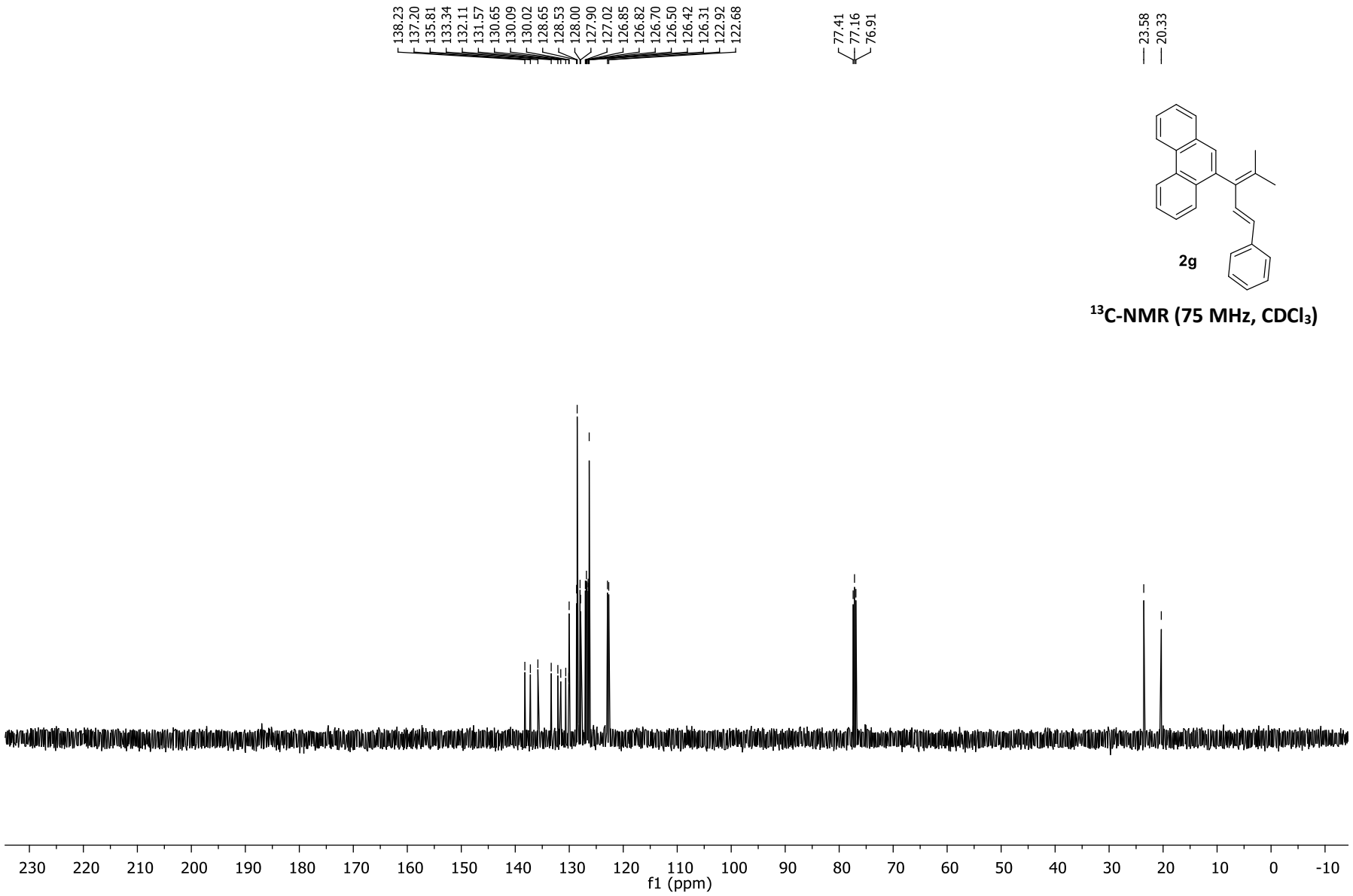
iso-3f

^{1}H-NMR (500 MHz, $CDCl_3$)

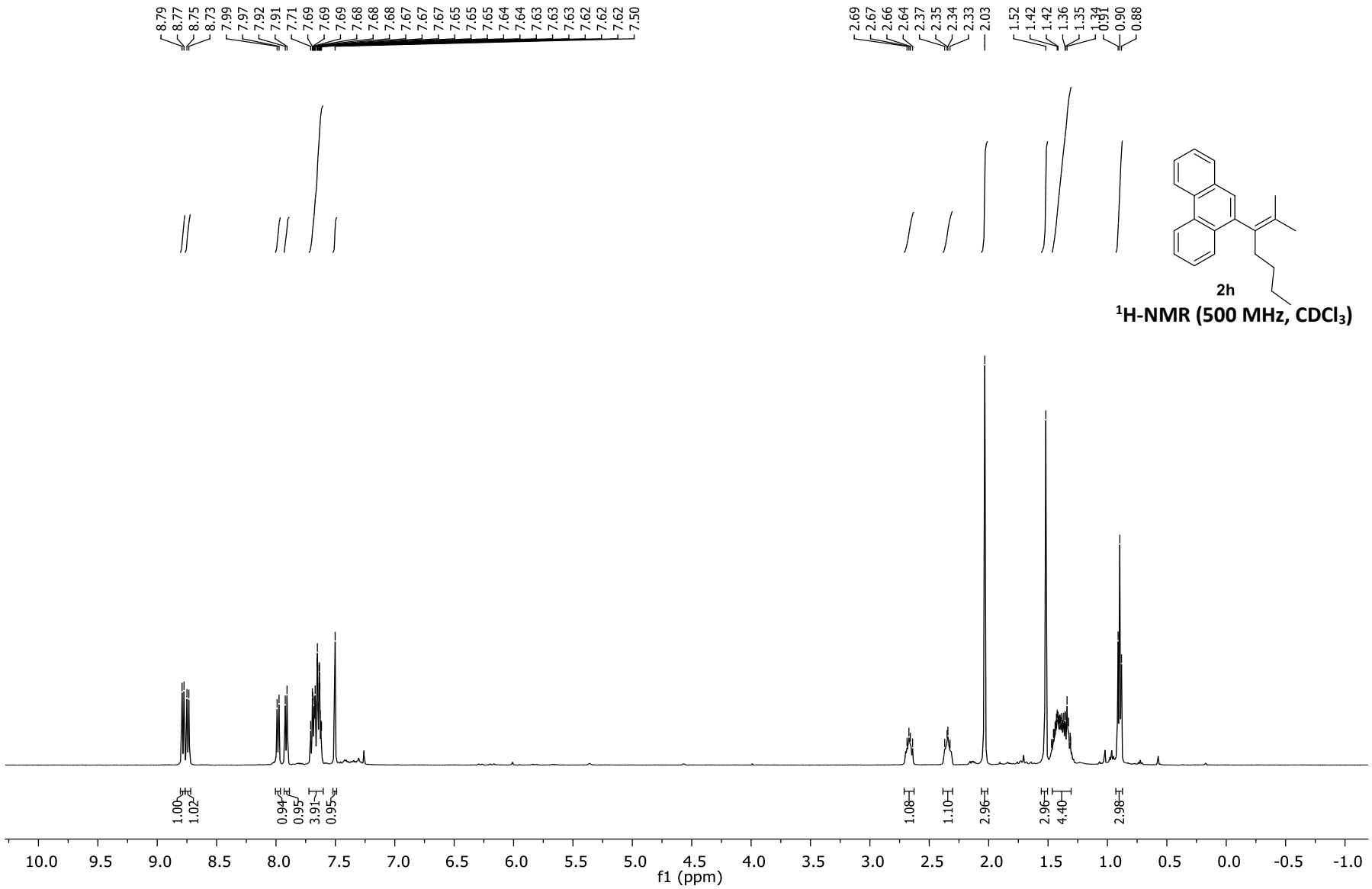

162.07
144.03
140.75
136.73
131.41
130.38
130.32
129.72
128.70
128.07
127.61
127.10
127.03
126.87
126.79
126.50
126.24
126.17
125.97
122.95
122.76
120.36
117.44
77.41
77.16
76.91
40.16
25.31
N
iso-3f
13C-NMR (125 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

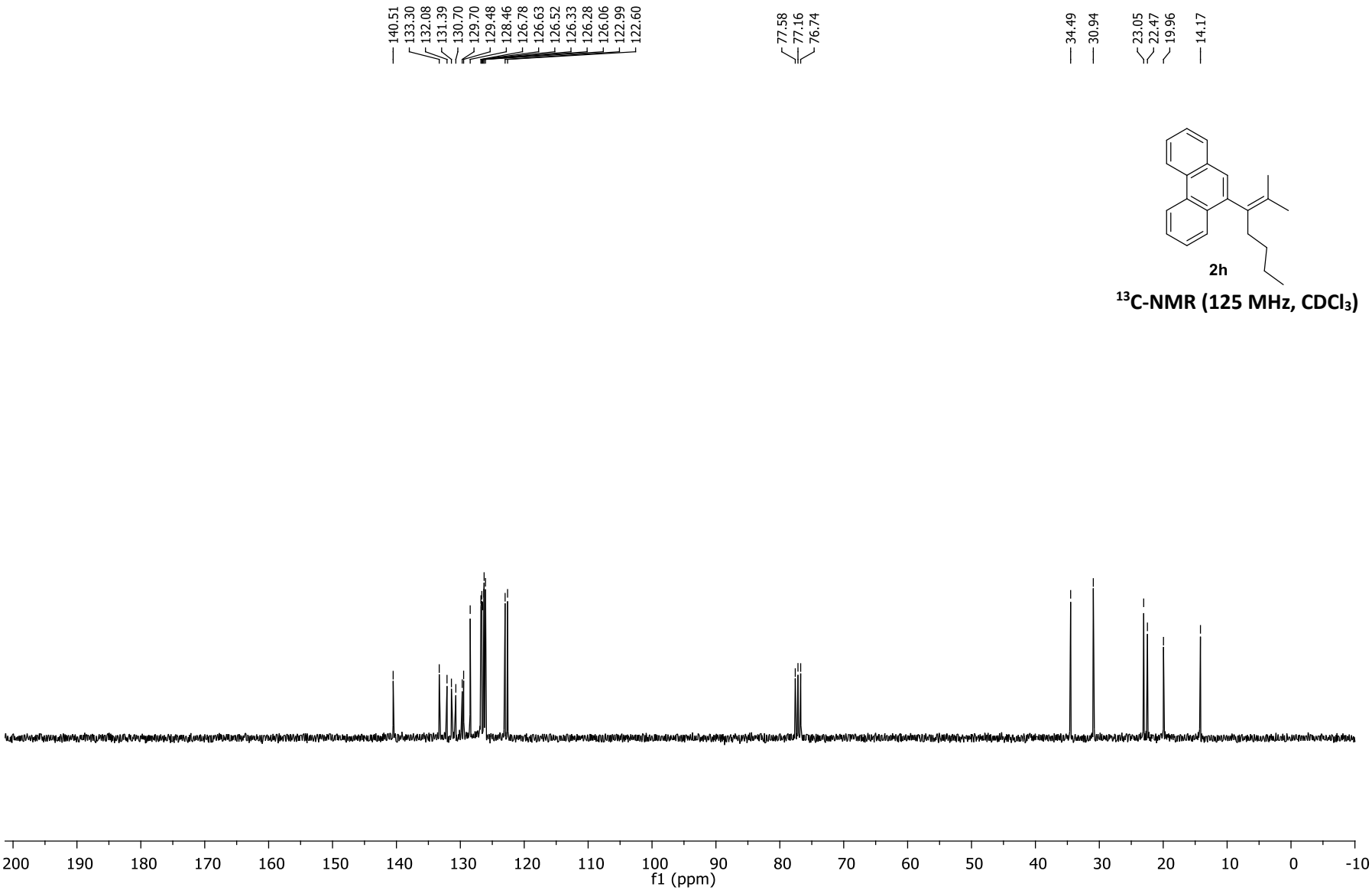


^{1}H-NMR (300 MHz, $CDCl_3$)



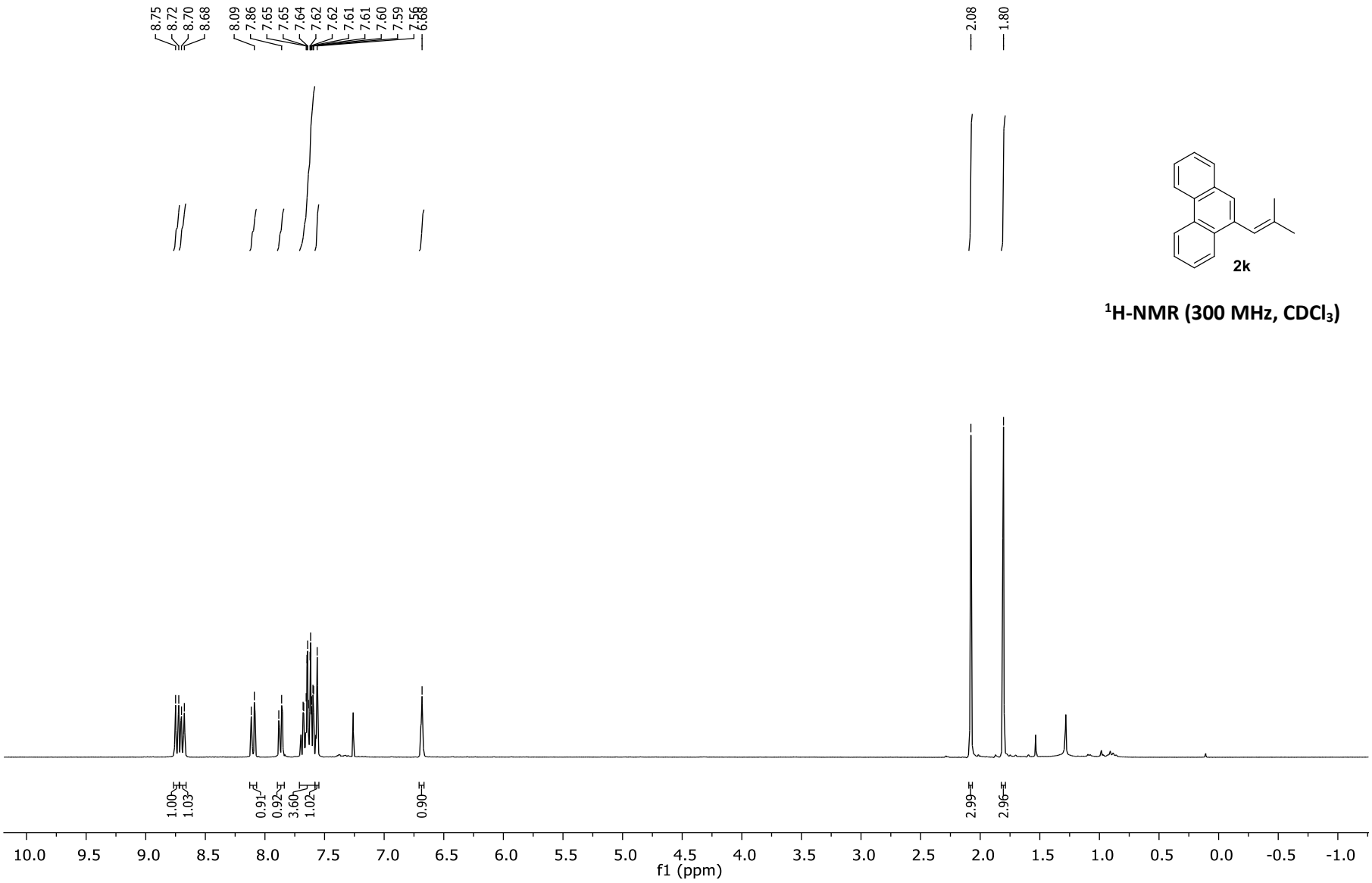
^{13}C-NMR (75 MHz, $CDCl_3$)


8.79
8.77
8.75
8.73
7.99
7.97
7.92
7.91
7.71
7.69
7.69
7.69
7.68
7.68
7.68
7.67
7.67
7.67
7.65
7.65
7.65
7.64
7.64
7.63
7.63
7.63
7.62
7.62
7.62
7.50
2.69
2.67
2.66
2.64
2.37
2.35
2.34
2.33
2.03
1.52
1.42
1.42
1.36
1.35
1.34
0.91
0.90
0.88
2h
1H-NMR (500 MHz, CDCl3)
1.00
1.02
0.94
0.95
3.91
0.95
1.08
1.10
2.96
2.96
4.40
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



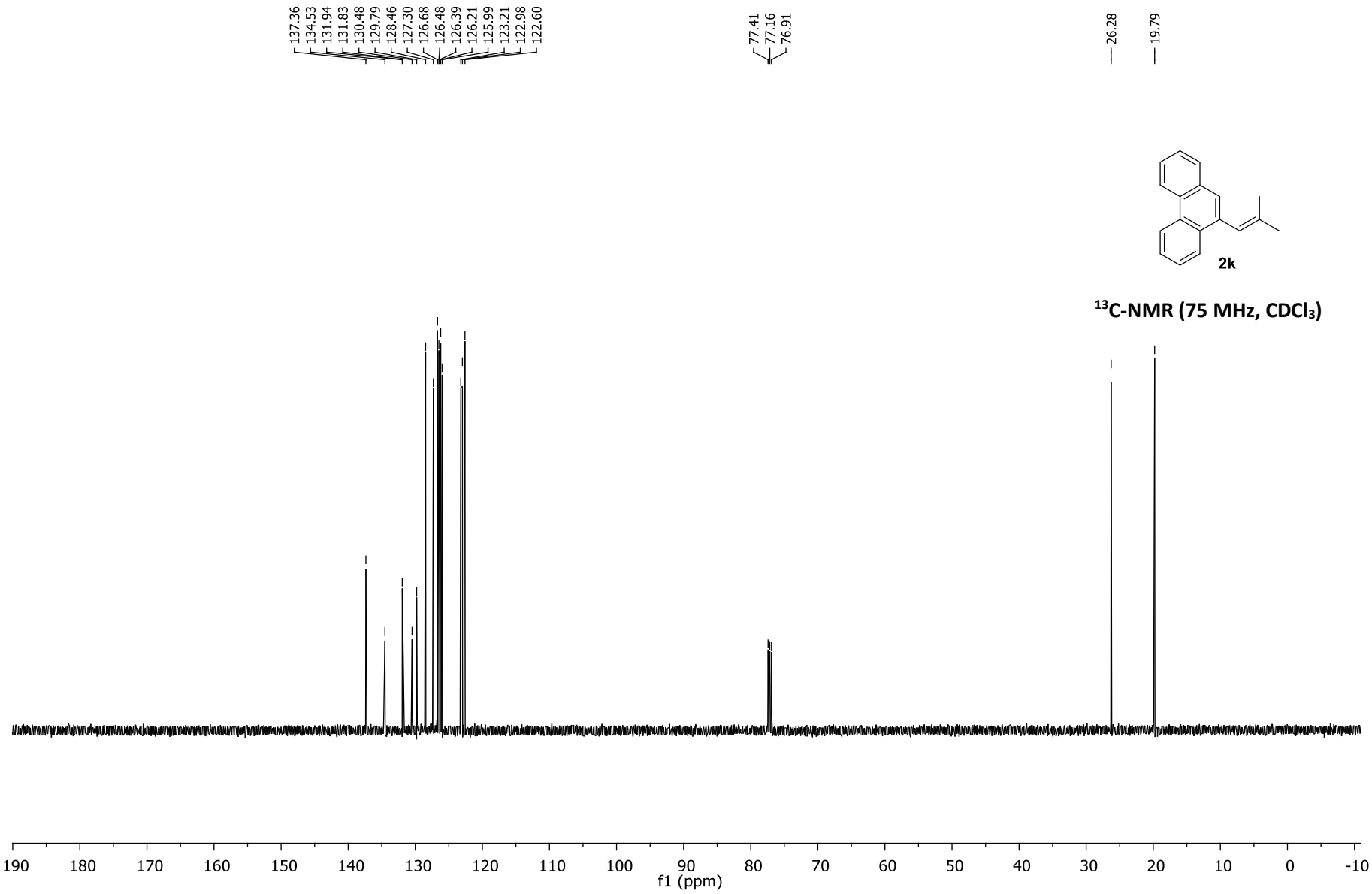
2h

^{13}C-NMR (125 MHz, $CDCl_3$)

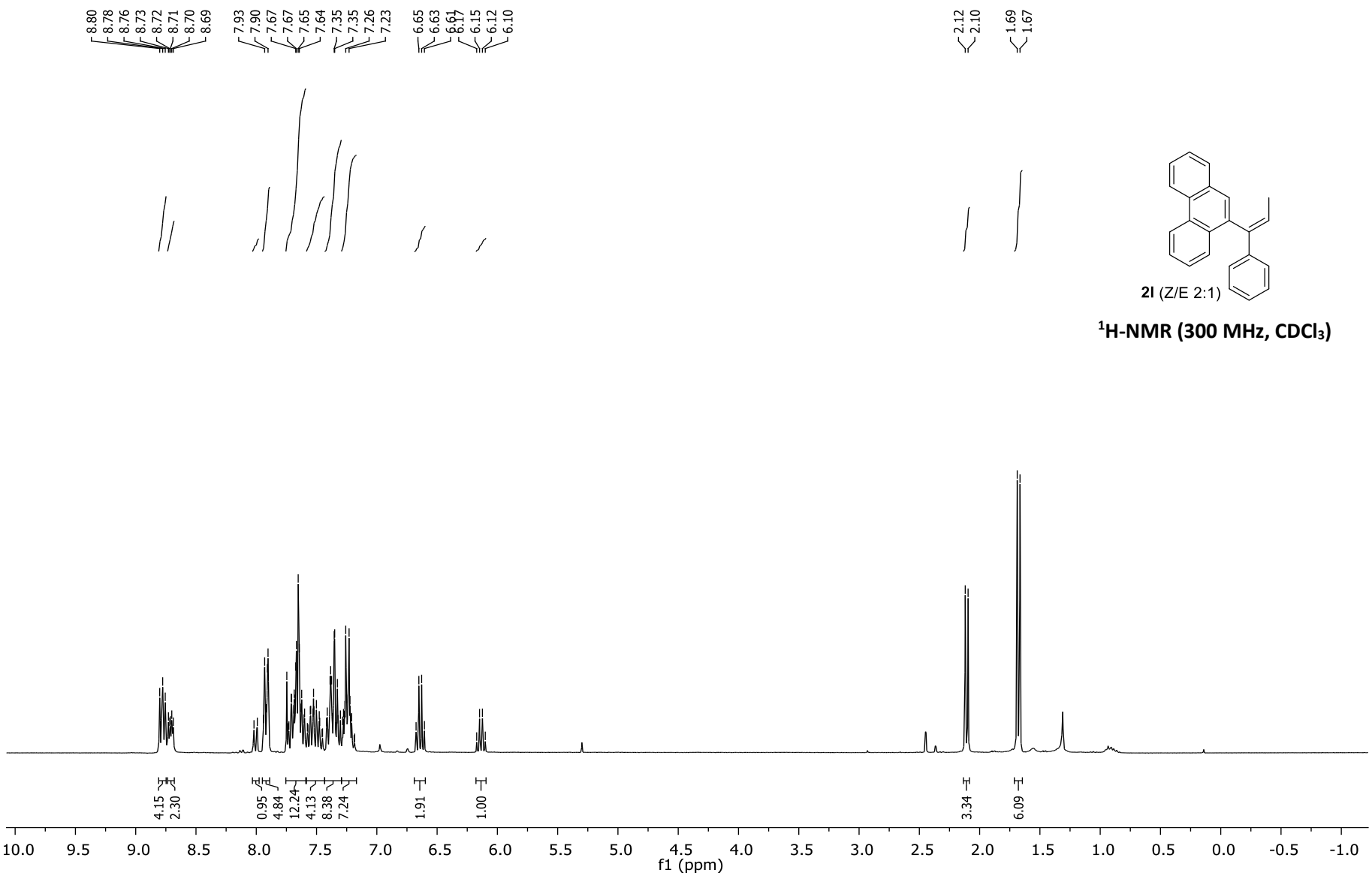


2k

^{1}H-NMR (300 MHz, $CDCl_3$)

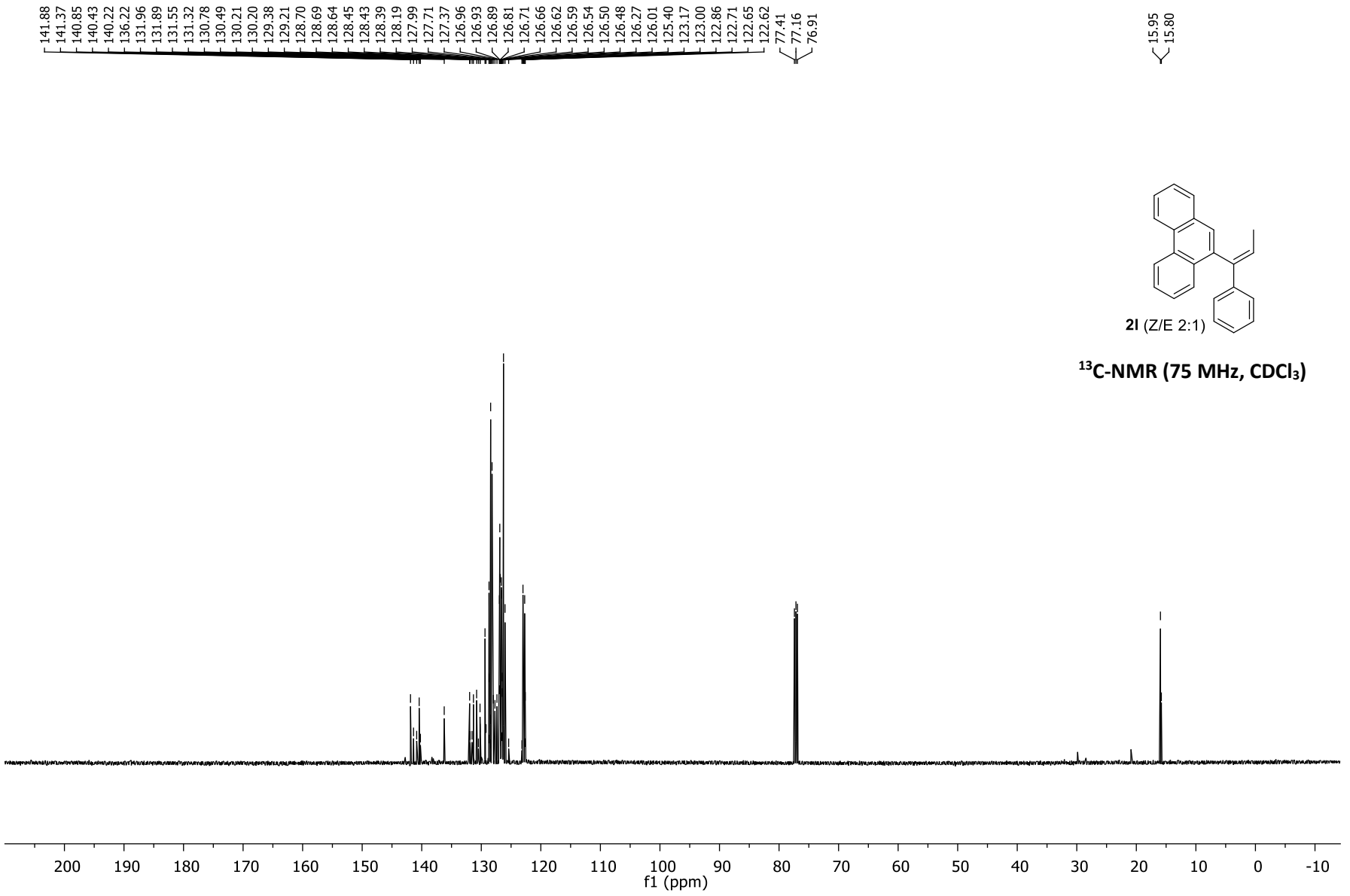


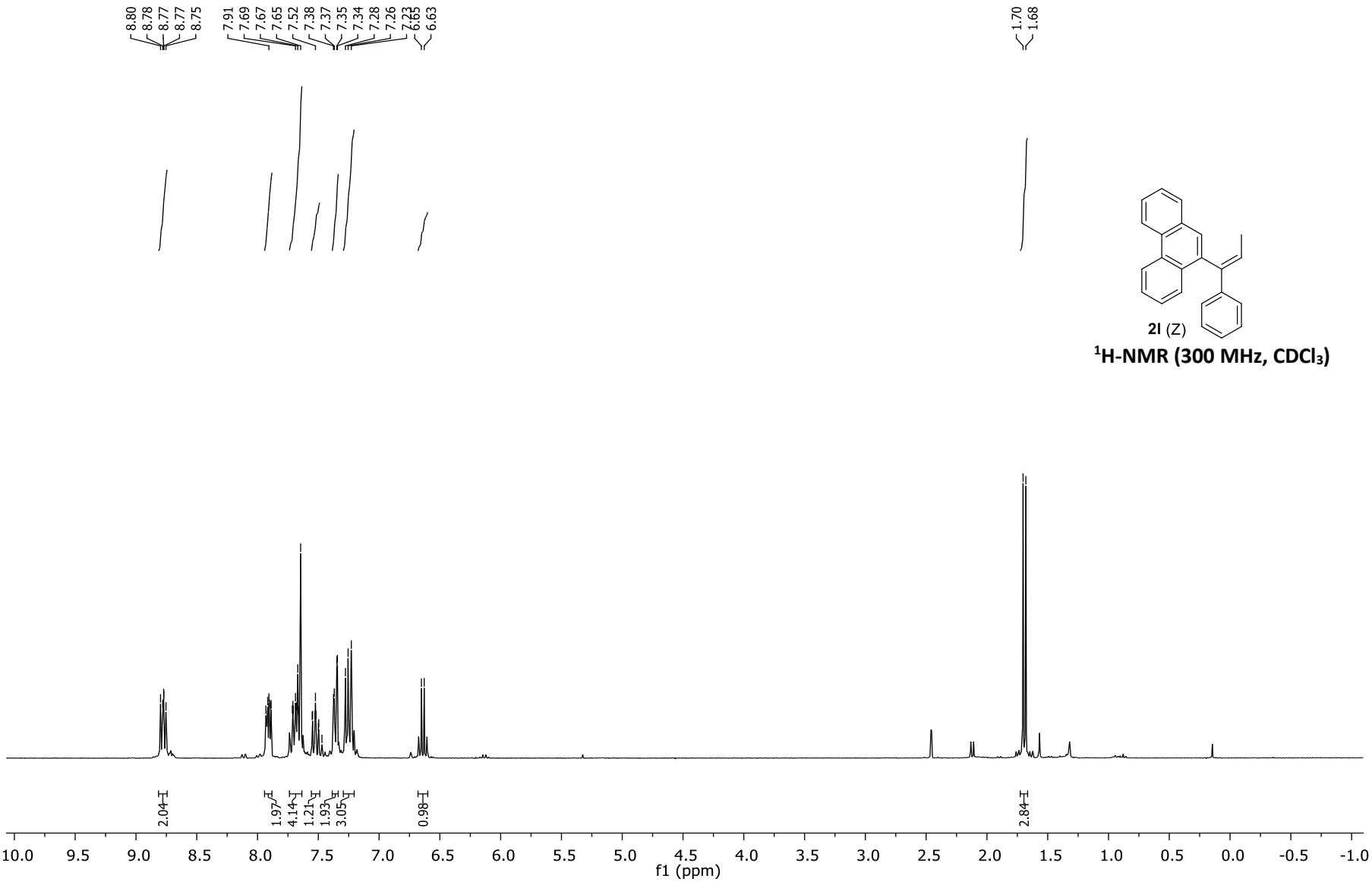
^{13}C-NMR (75 MHz, $CDCl_3$)



2l (Z/E 2:1)

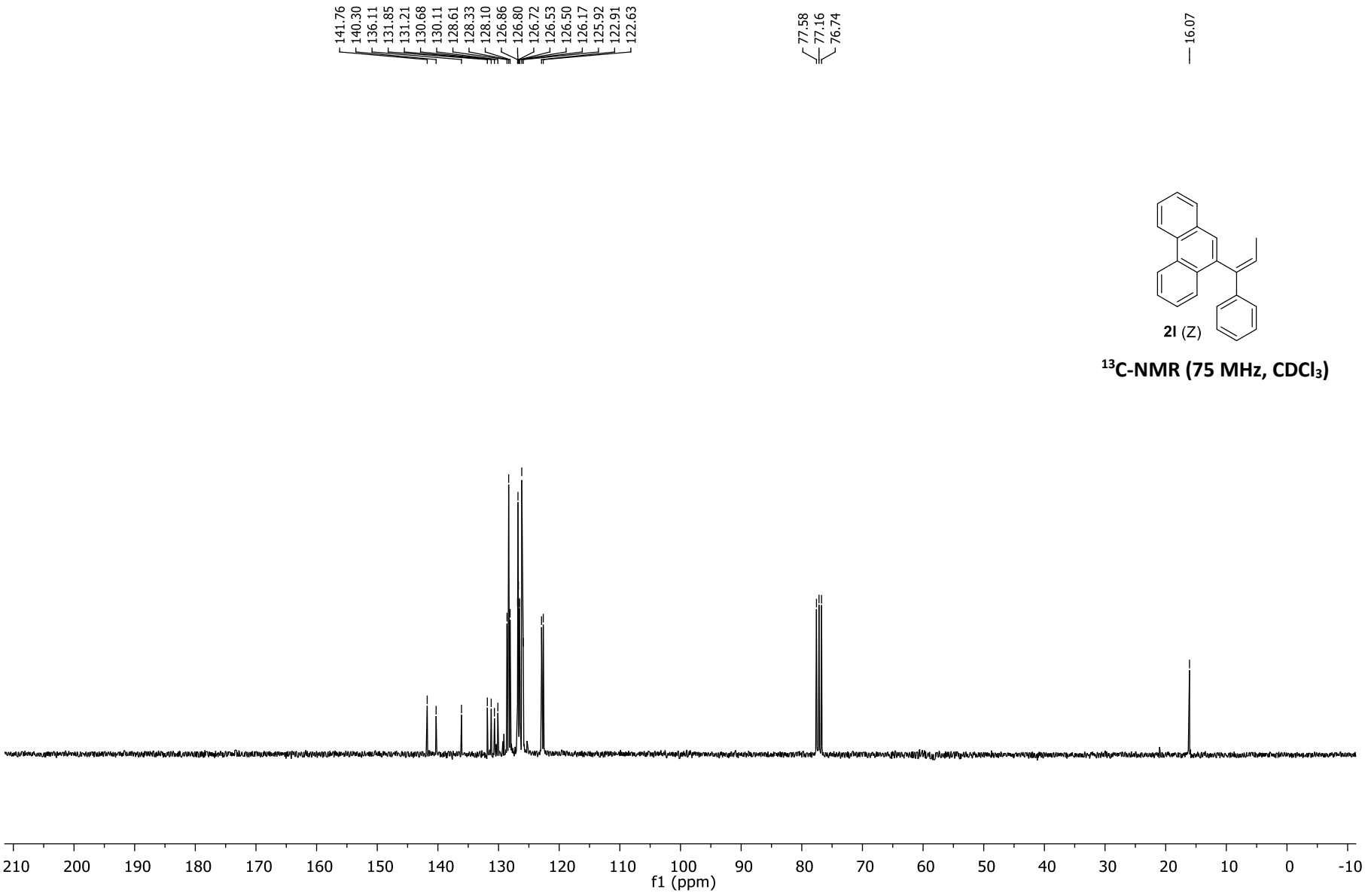
^{1}H-NMR (300 MHz, $CDCl_3$)


141.88
141.37
140.85
140.43
140.22
136.22
131.96
131.89
131.55
131.32
130.78
130.49
130.21
130.20
129.38
129.21
128.70
128.69
128.64
128.45
128.43
128.39
128.19
127.99
127.71
127.37
126.96
126.93
126.89
126.81
126.71
126.66
126.62
126.59
126.54
126.50
126.48
126.27
126.01
125.40
123.17
123.00
122.86
122.71
122.65
122.62
77.41
77.16
76.91
15.95
15.80
2l (Z/E 2:1)
13C-NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

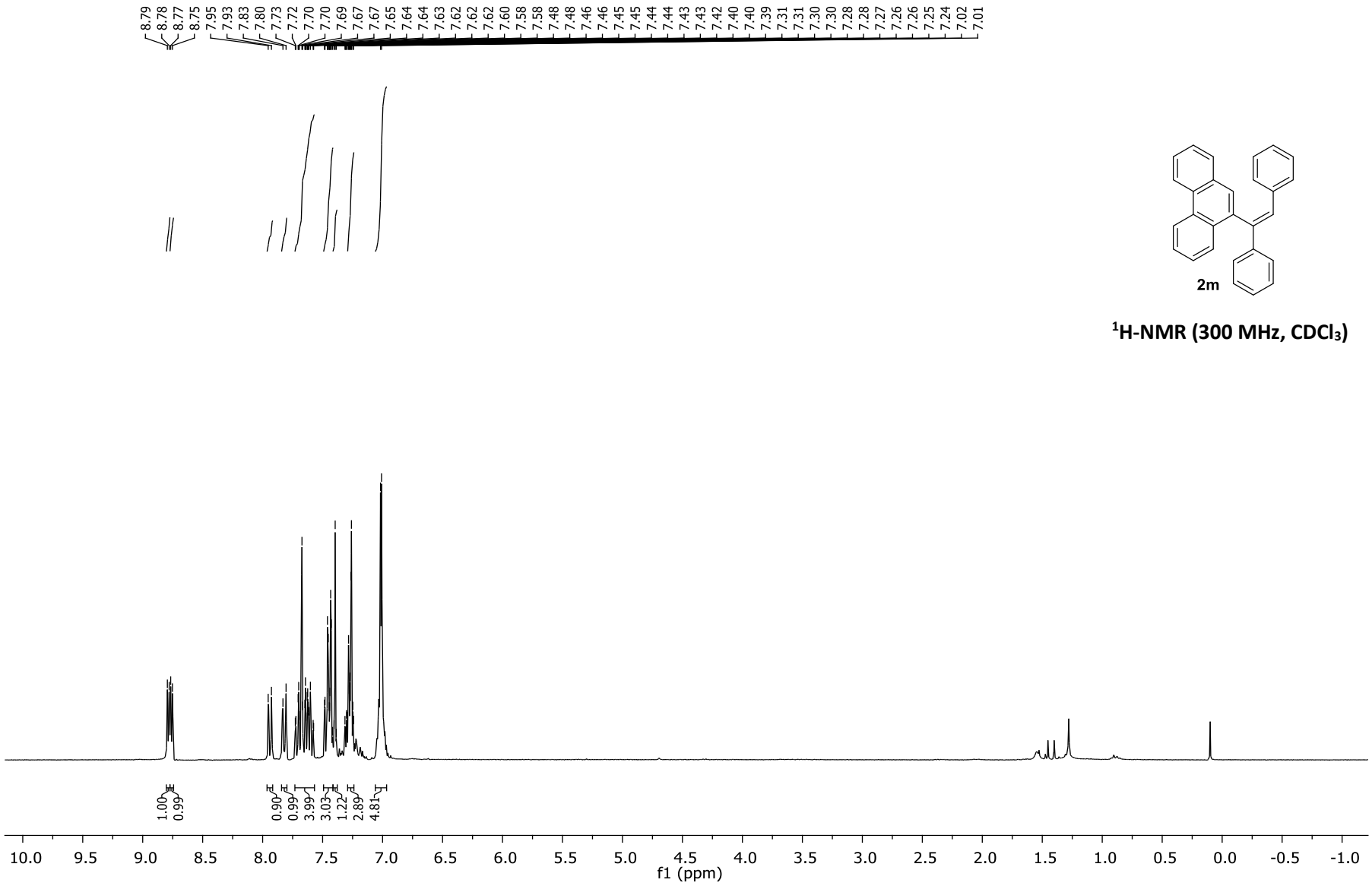


2l (Z)

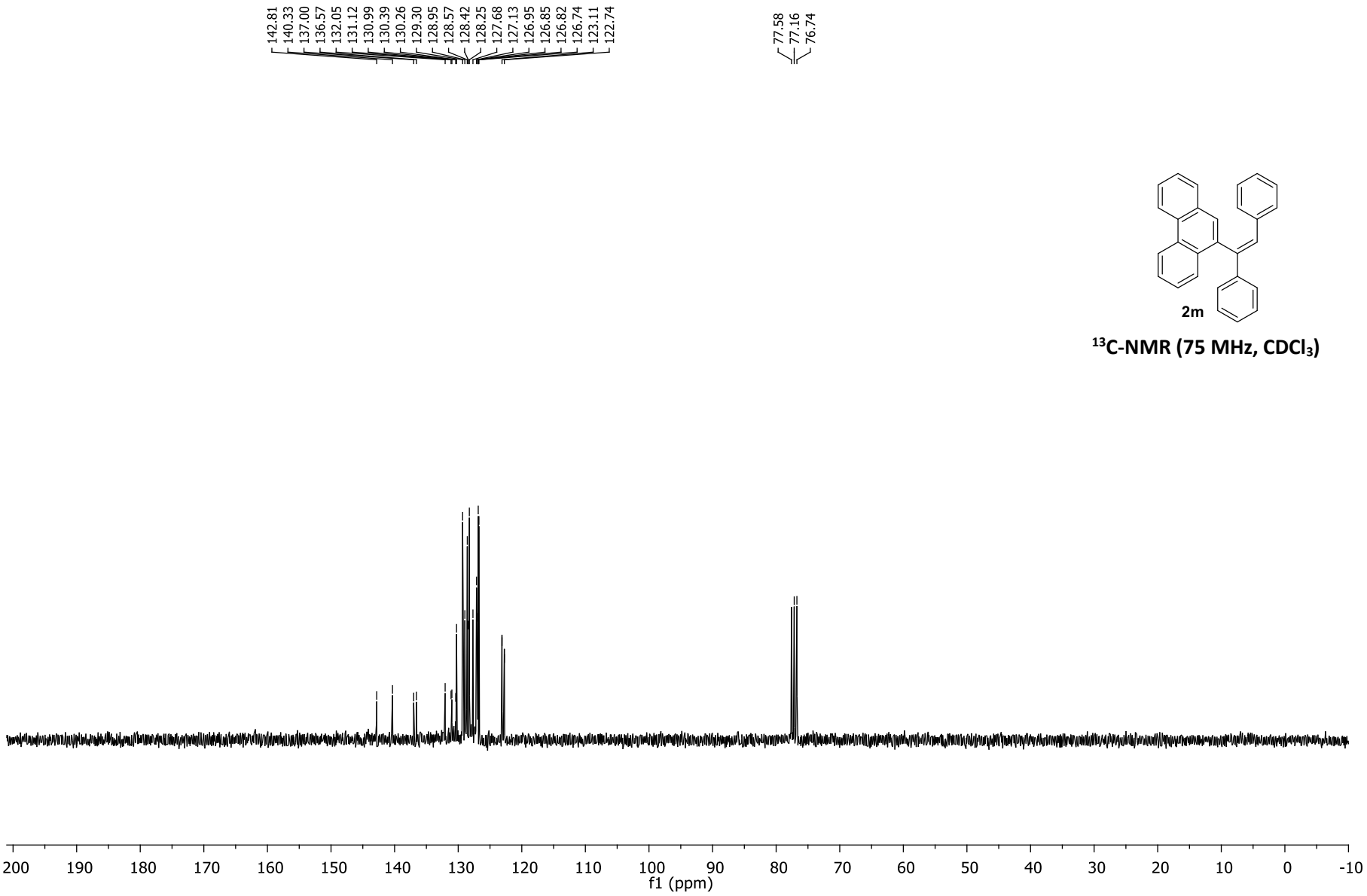
^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (75 MHz, $CDCl_3$)

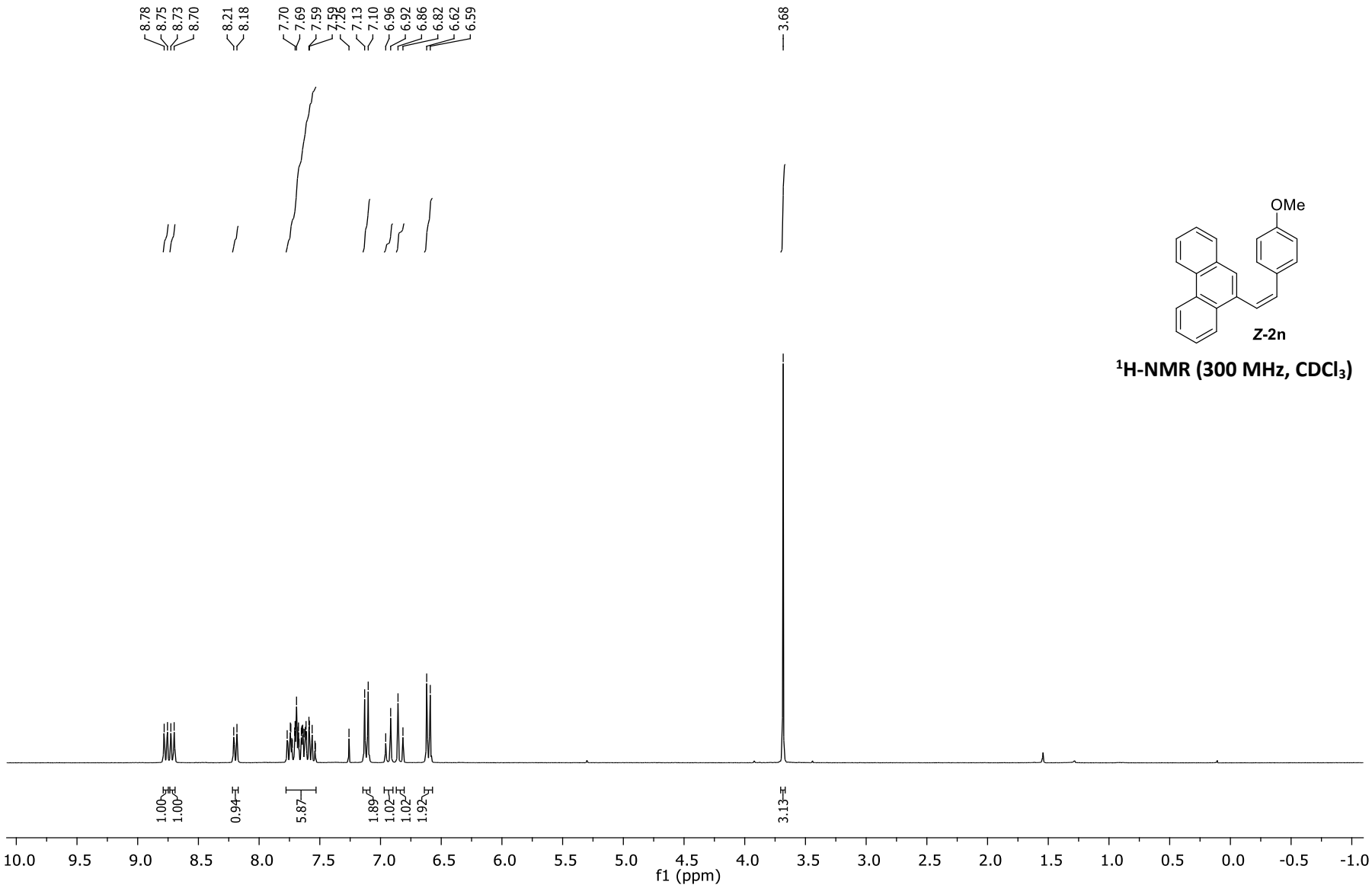


^{1}H-NMR (300 MHz, $CDCl_3$)

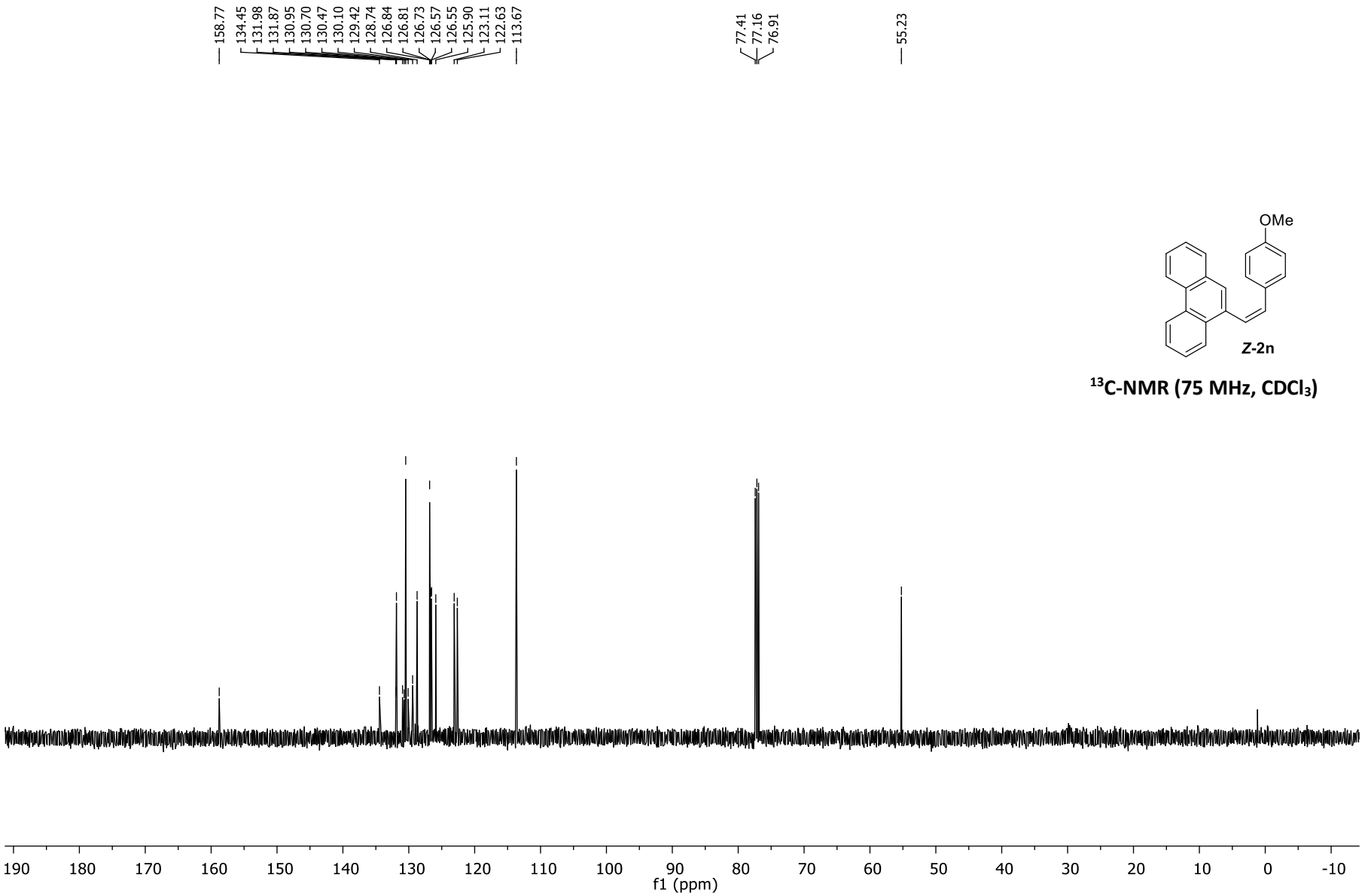


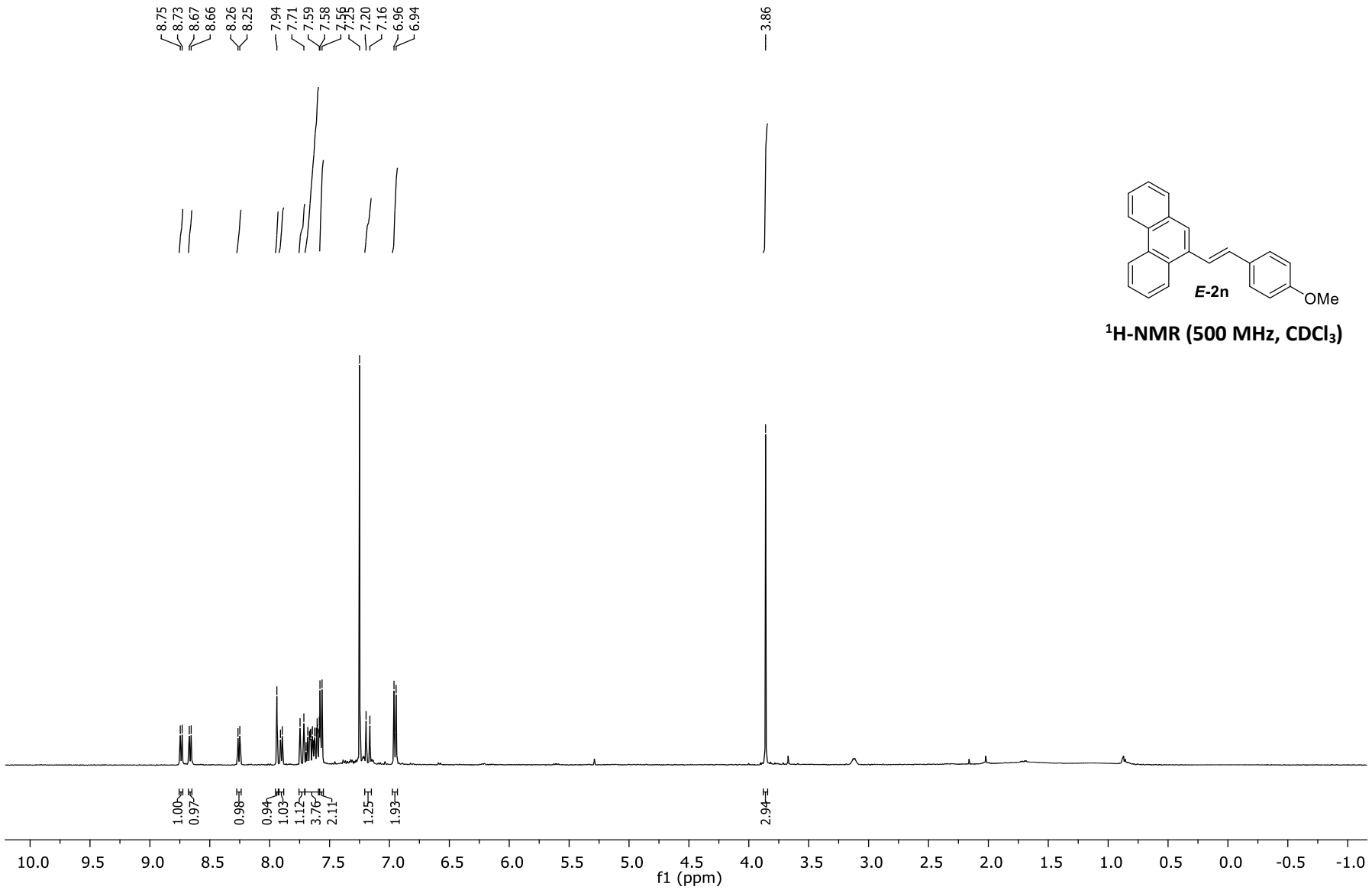
2m

^{13}C-NMR (75 MHz, $CDCl_3$)

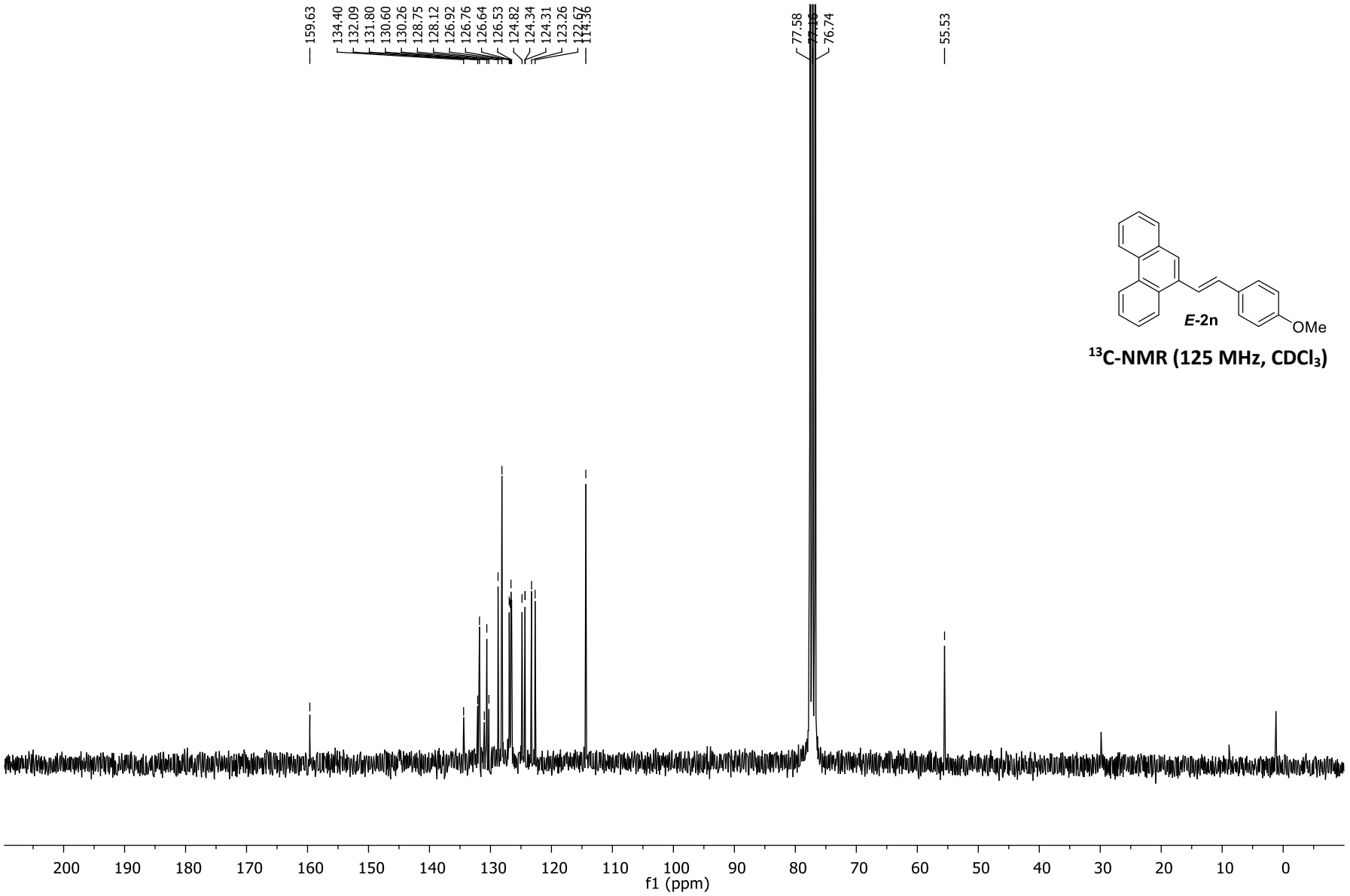


^{1}H-NMR (300 MHz, $CDCl_3$)


158.77
134.45
131.98
131.87
130.95
130.70
130.47
130.10
129.42
128.74
126.84
126.81
126.73
126.57
126.55
125.90
123.11
122.63
113.67
77.41
77.16
76.91
55.23
OMe
Z-2n
13C-NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

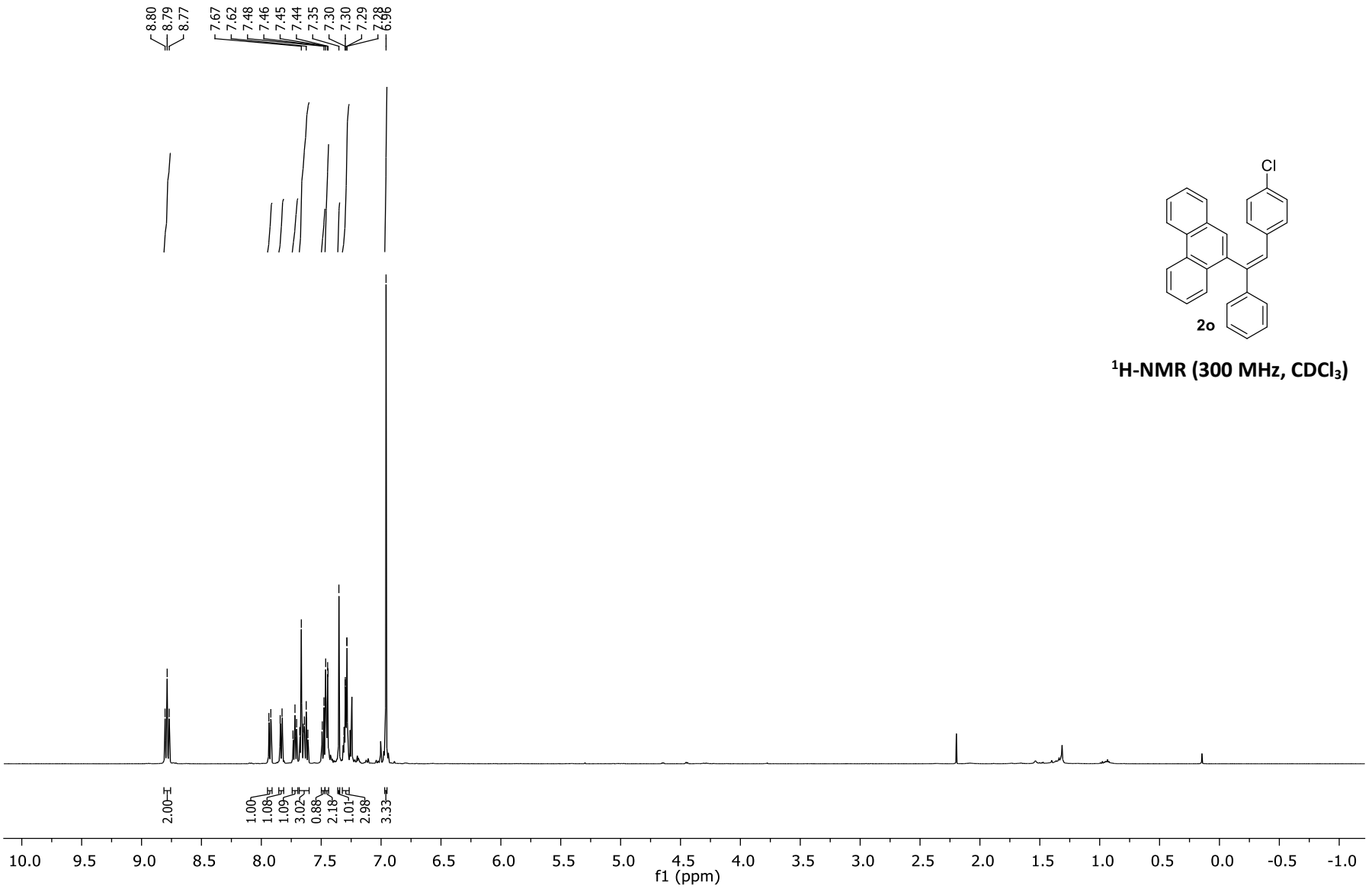


^{1}H-NMR (500 MHz, $CDCl_3$)



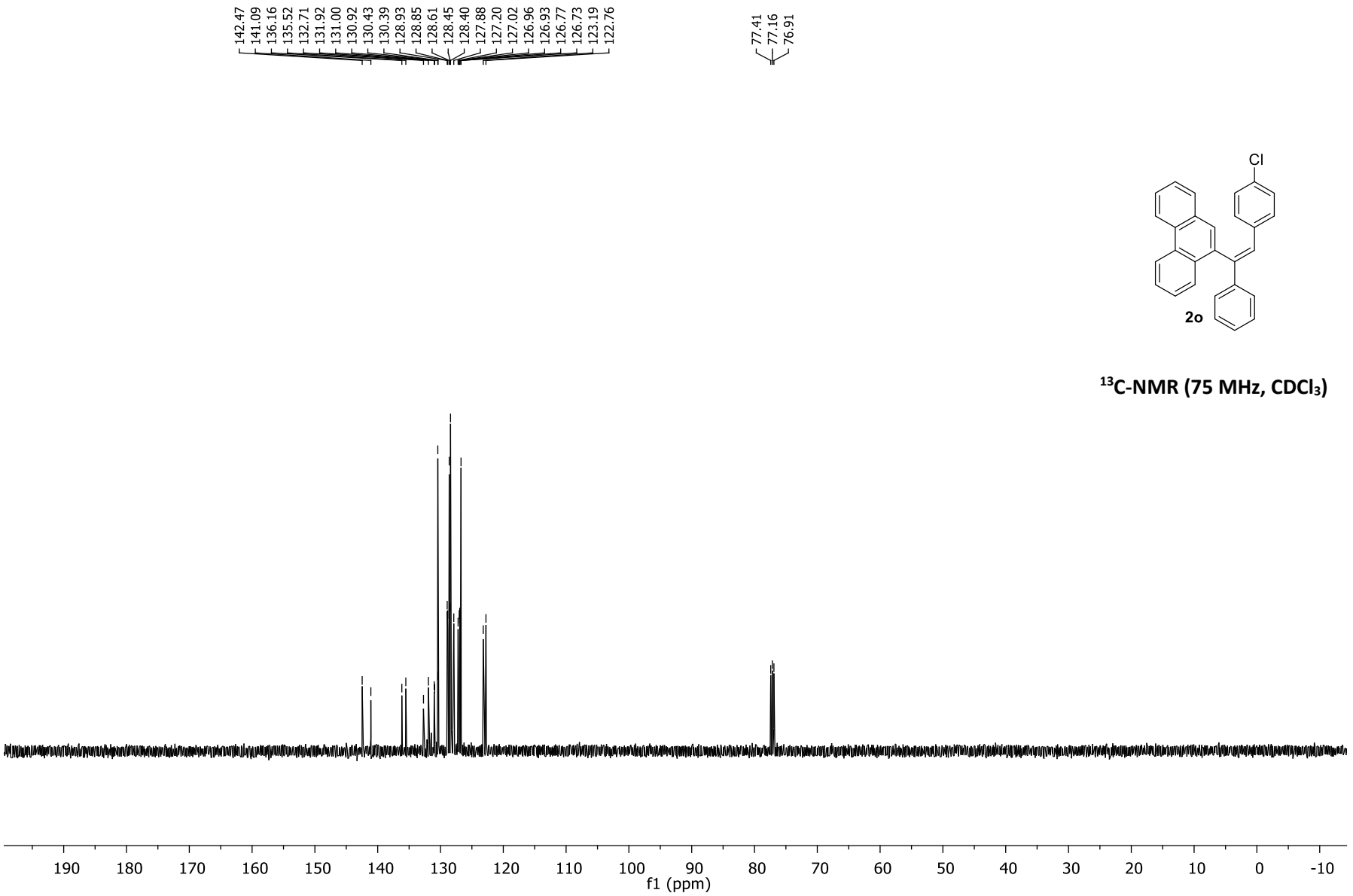
***E*-2n**

^{13}C-NMR (125 MHz, $CDCl_3$)

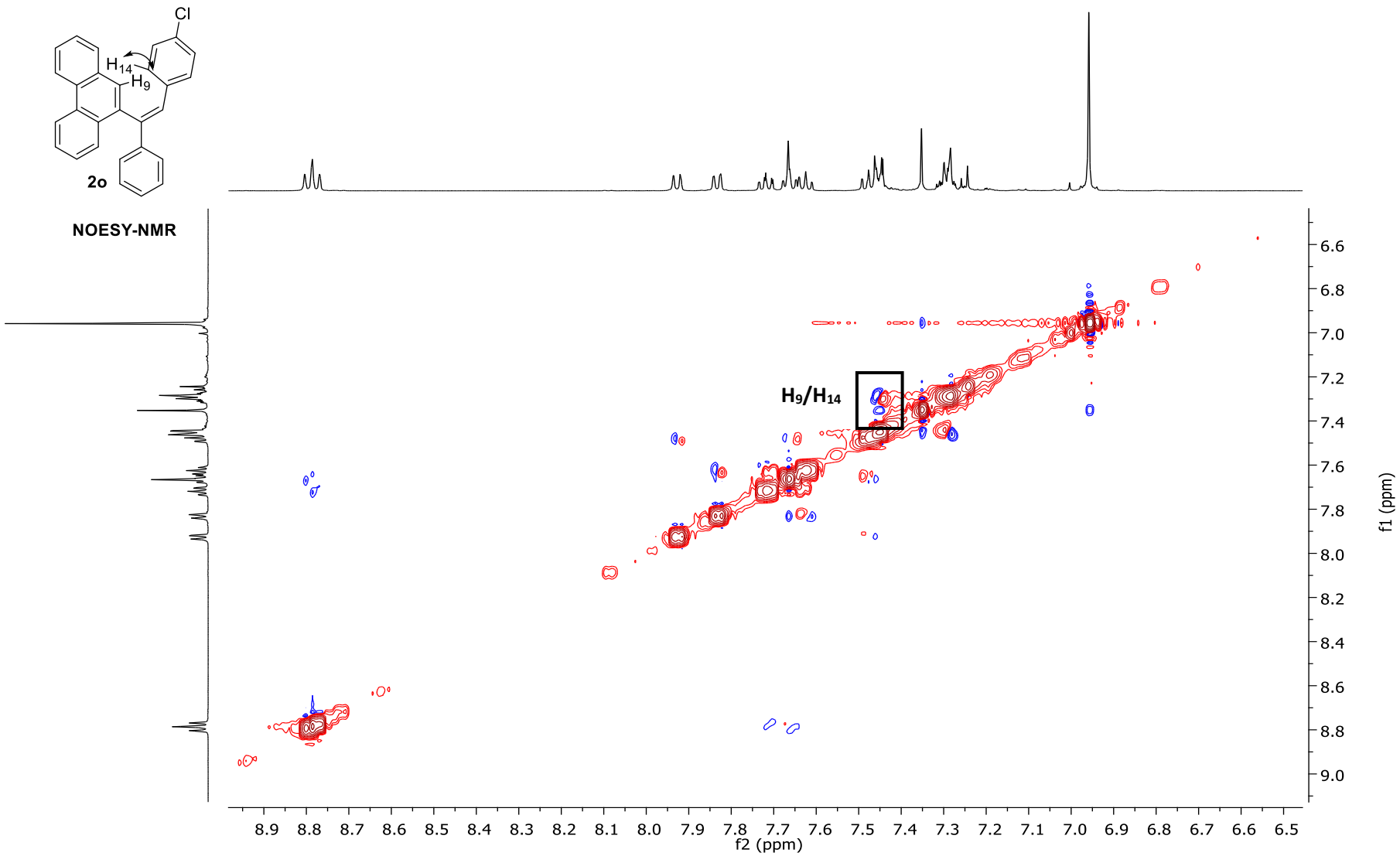


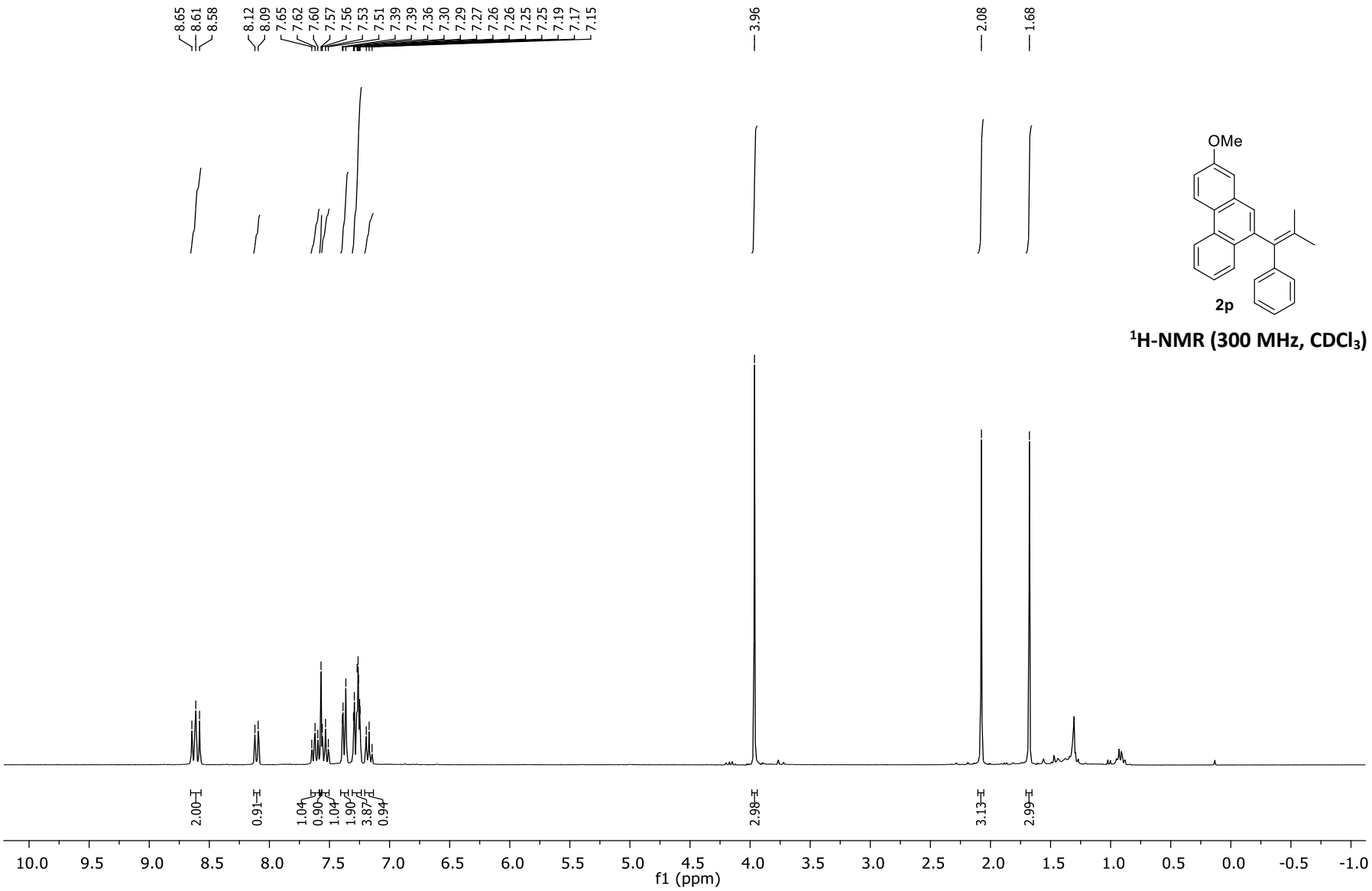
2o

^{1}H-NMR (300 MHz, $CDCl_3$)

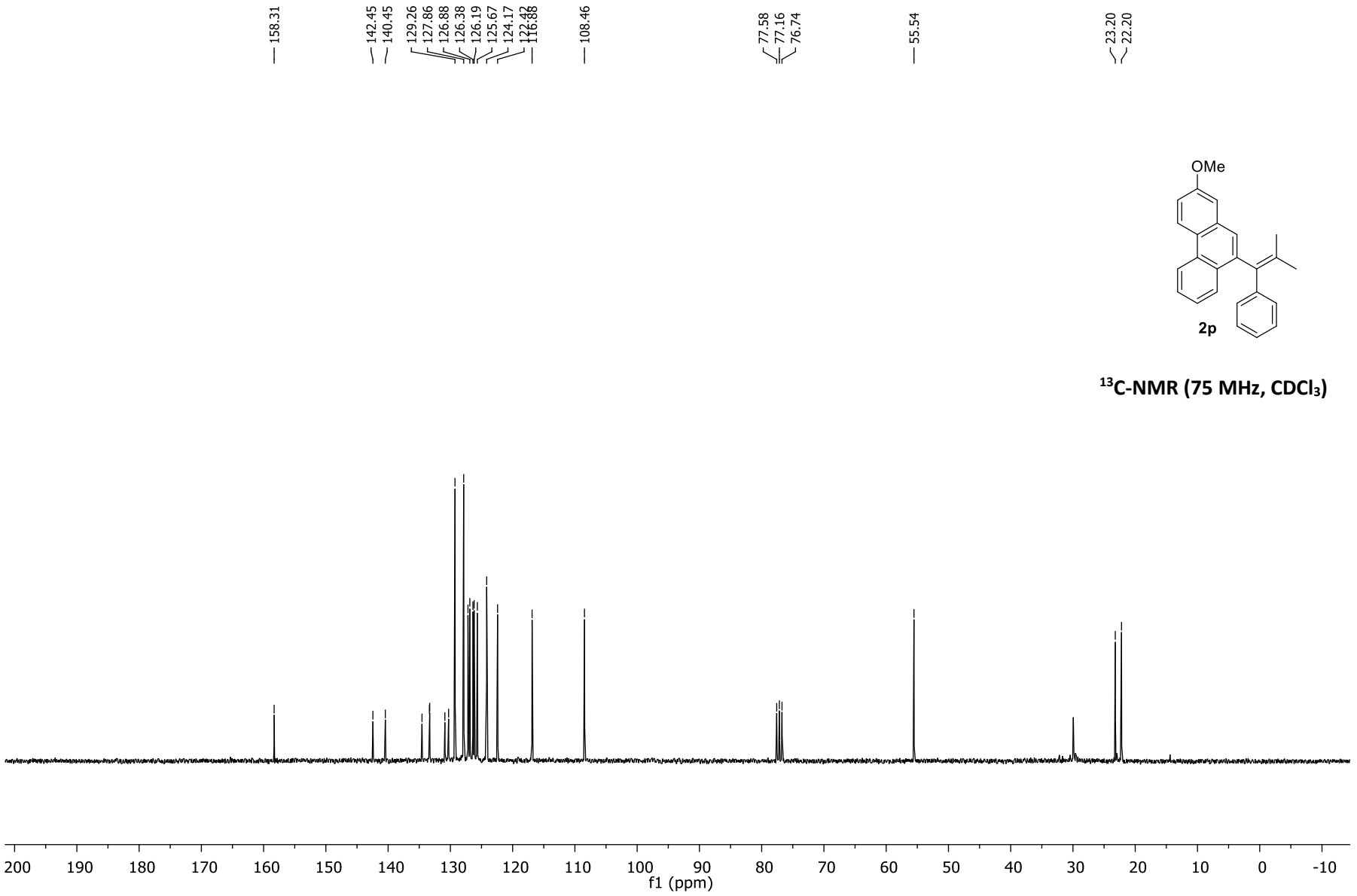


^{13}C-NMR (75 MHz, $CDCl_3$)

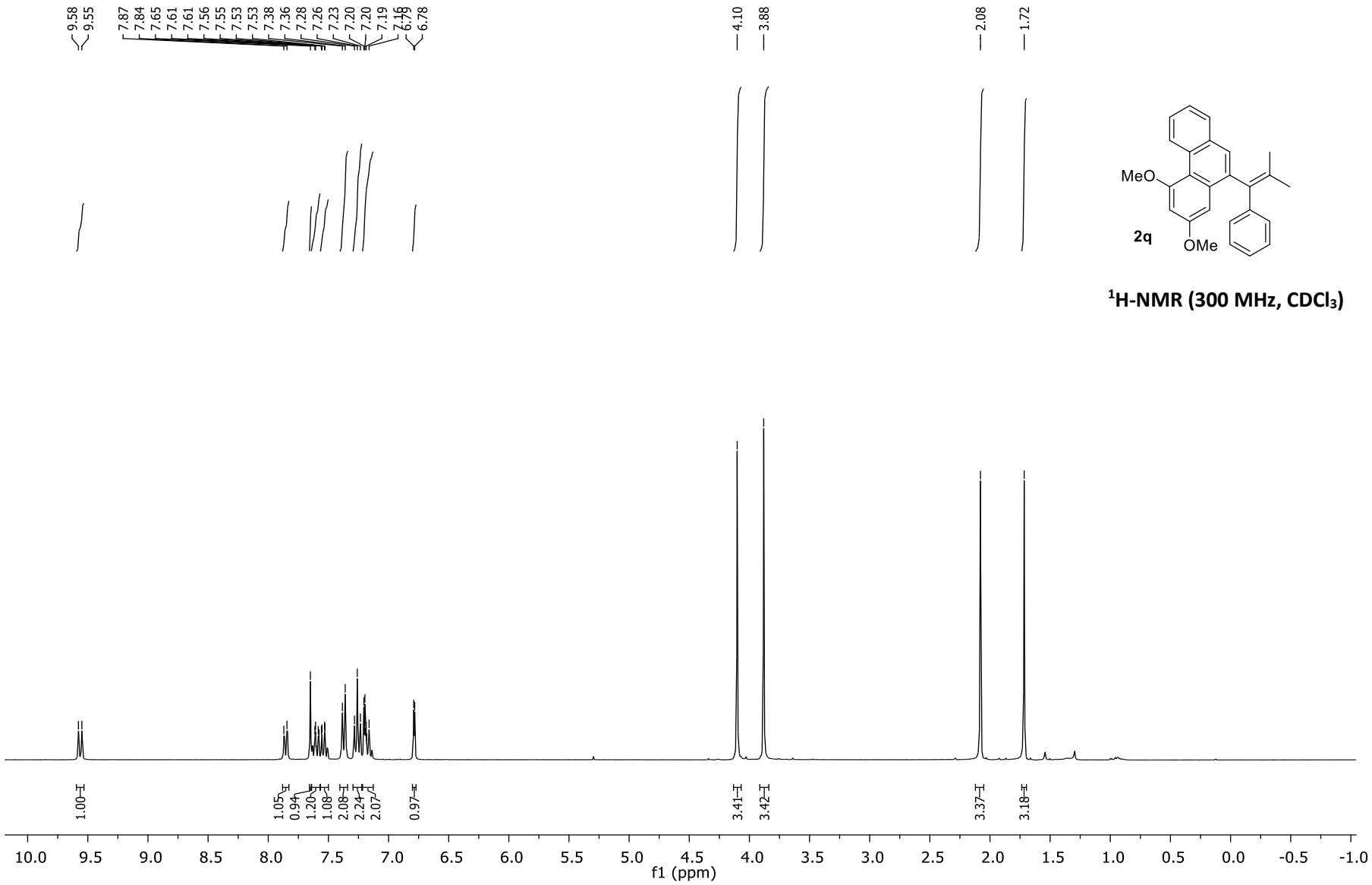

Cl
H14
H9
2o
NOESY-NMR
H9/H14
f2 (ppm)
f1 (ppm)



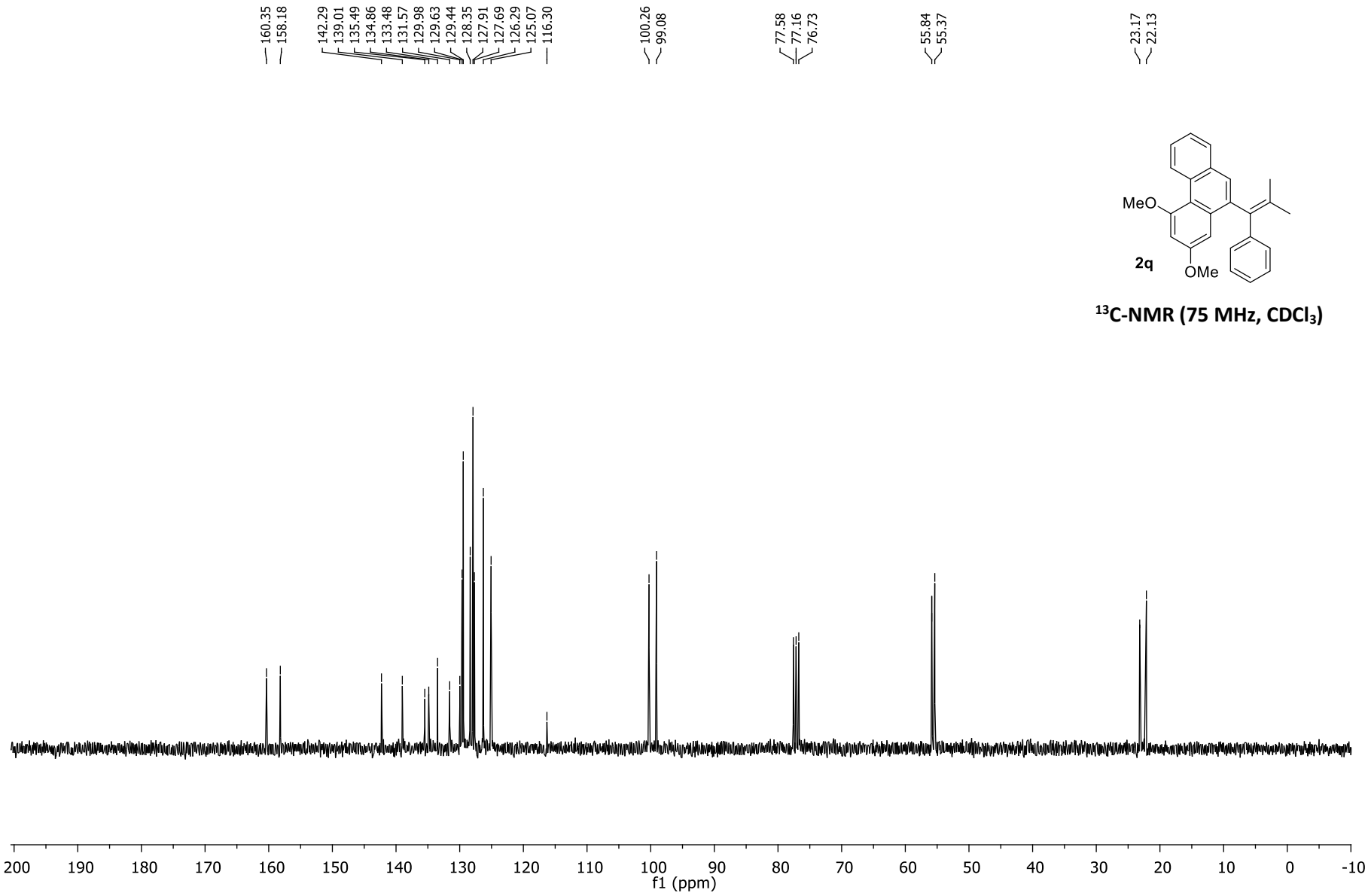
^{1}H-NMR (300 MHz, $CDCl_3$)



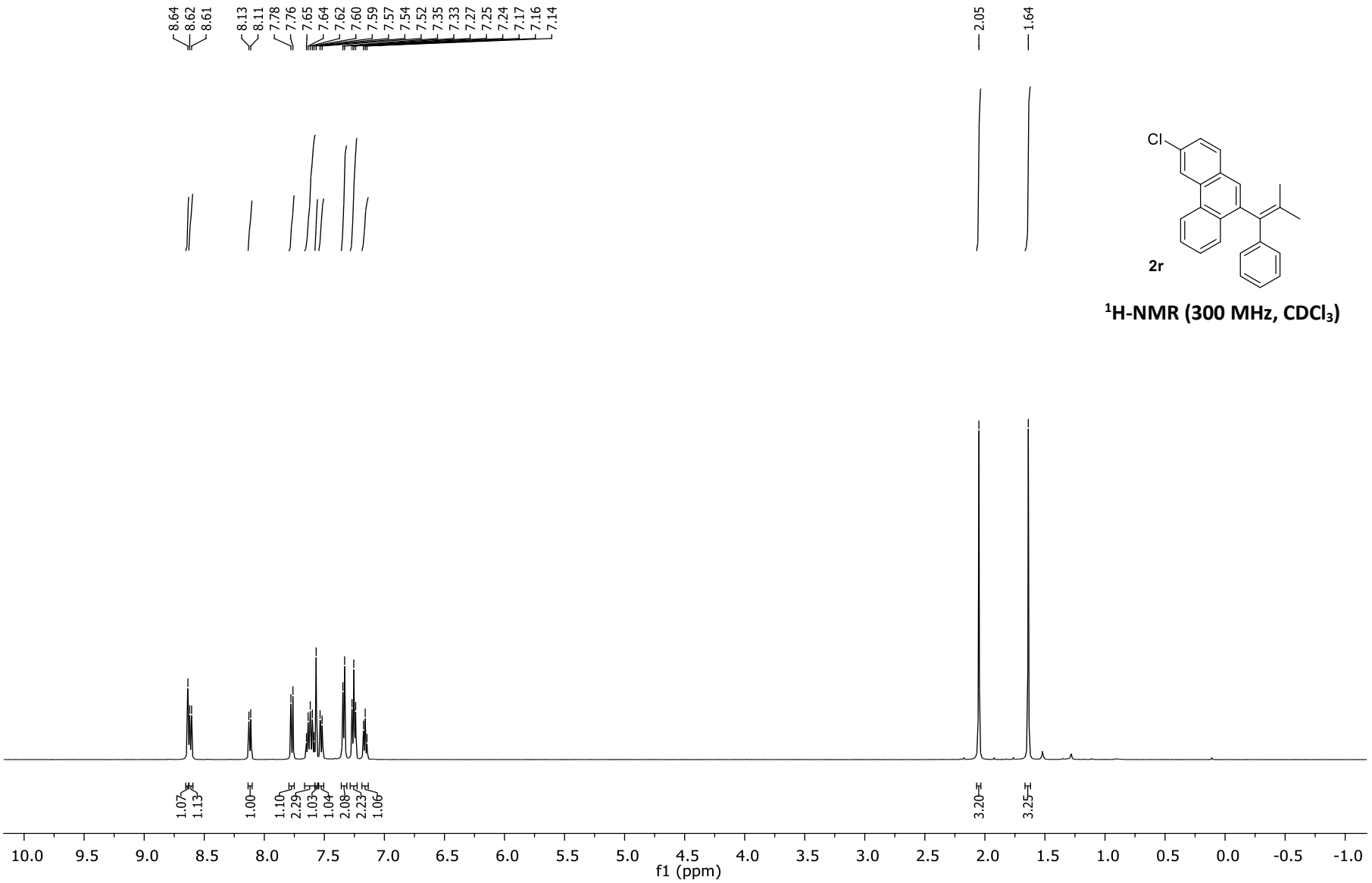
^{13}C-NMR (75 MHz, $CDCl_3$)



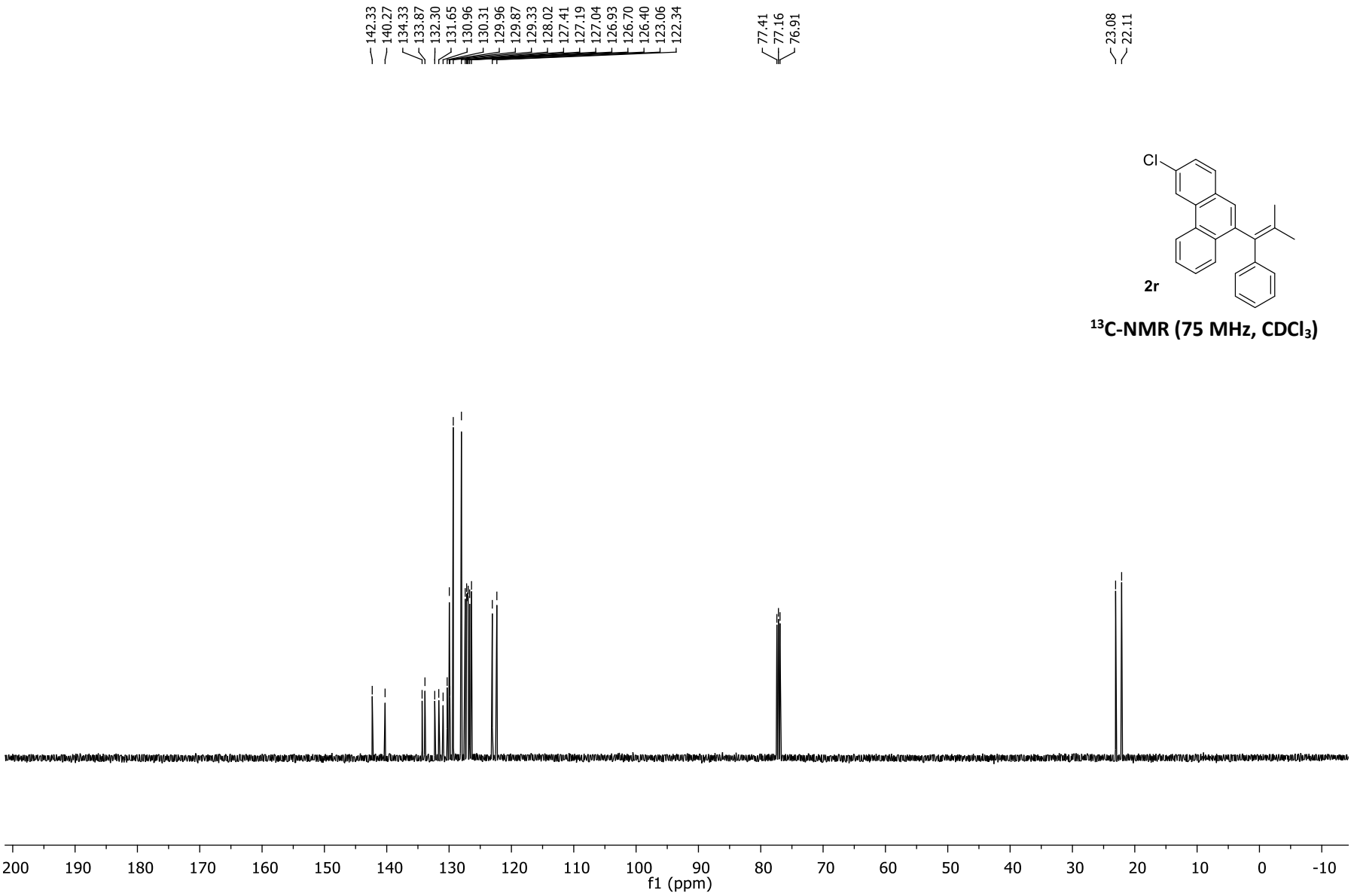
^{1}H-NMR (300 MHz, $CDCl_3$)



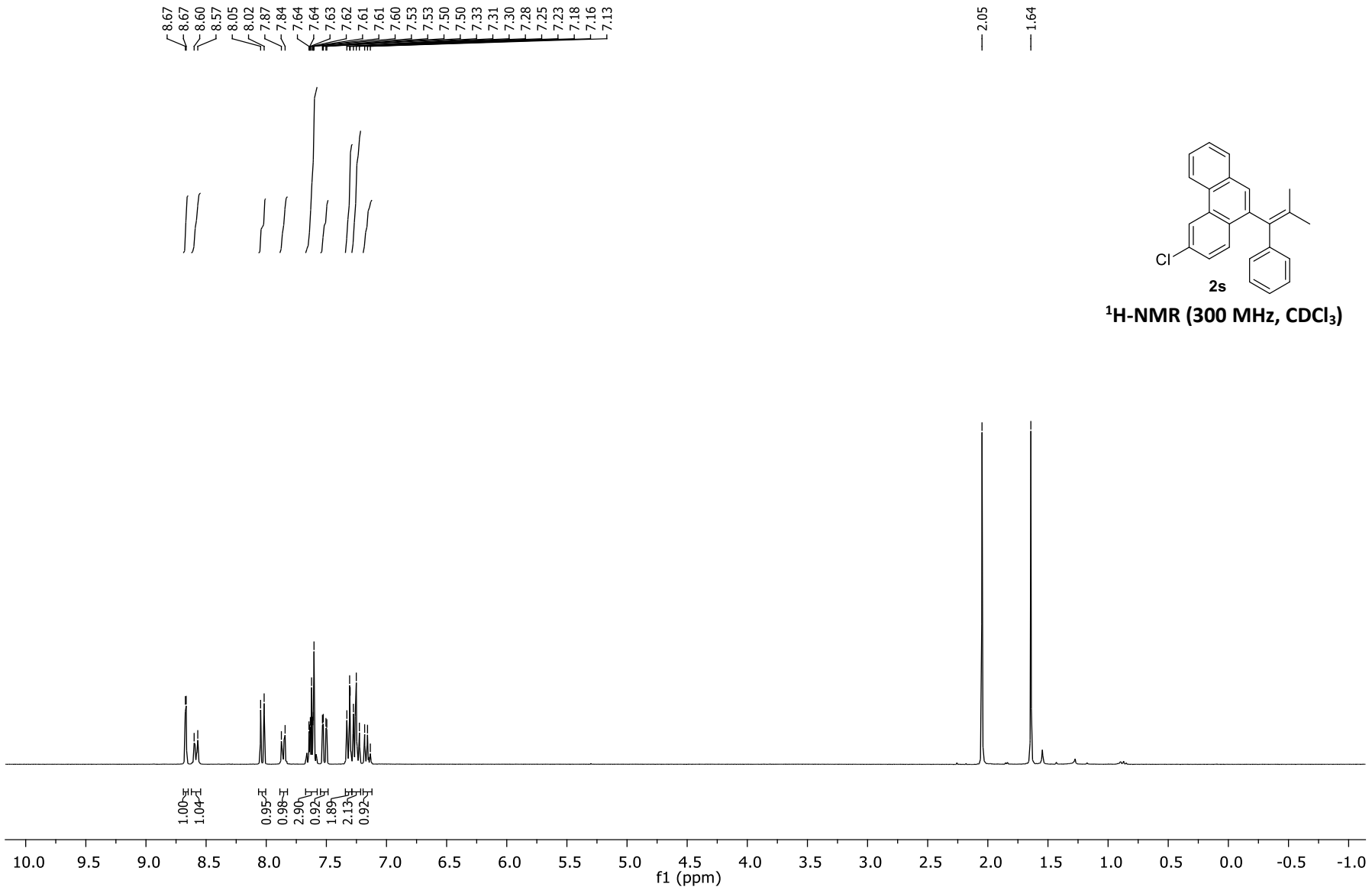
^{13}C-NMR (75 MHz, $CDCl_3$)



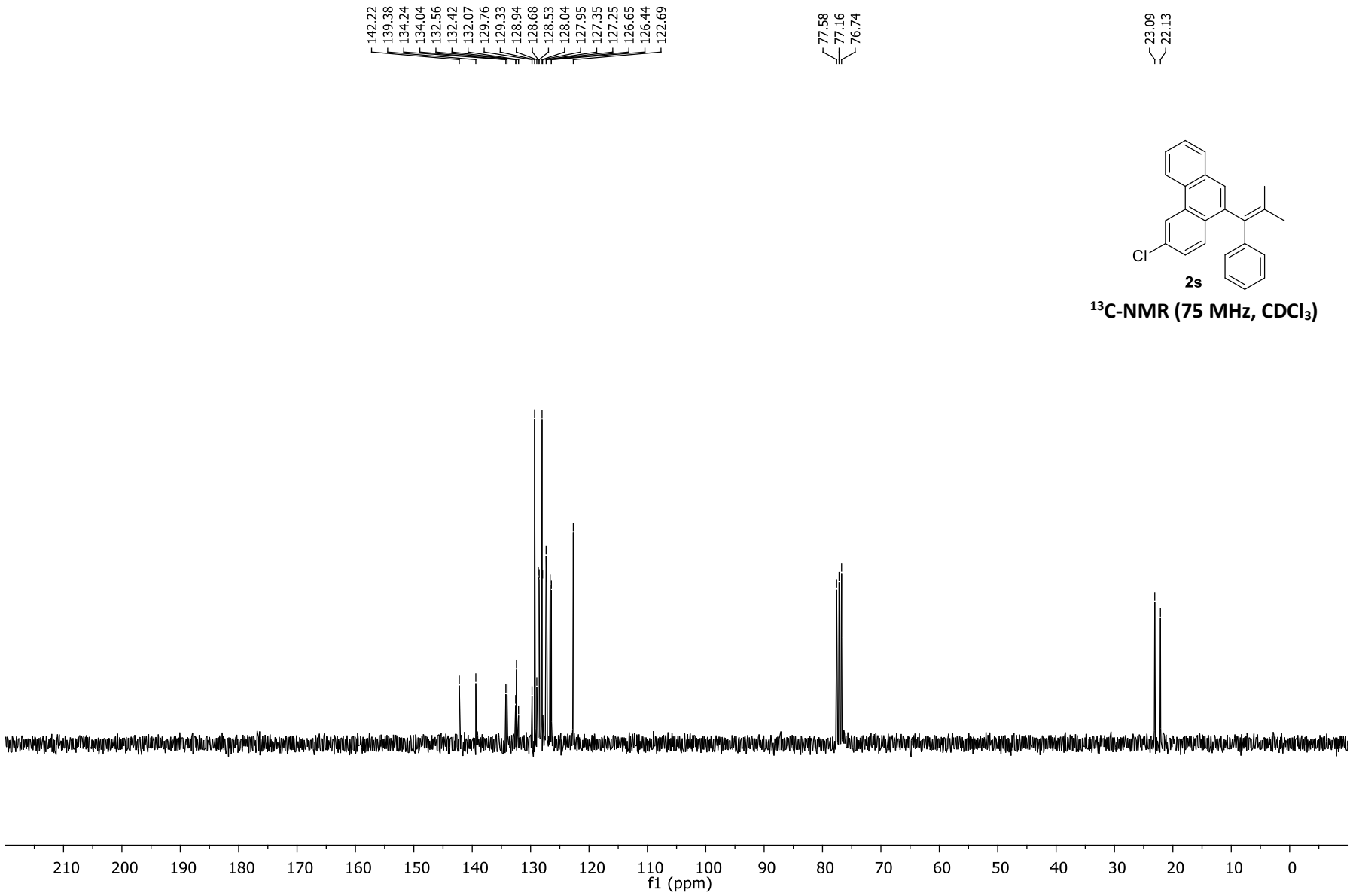
^{1}H-NMR (300 MHz, $CDCl_3$)



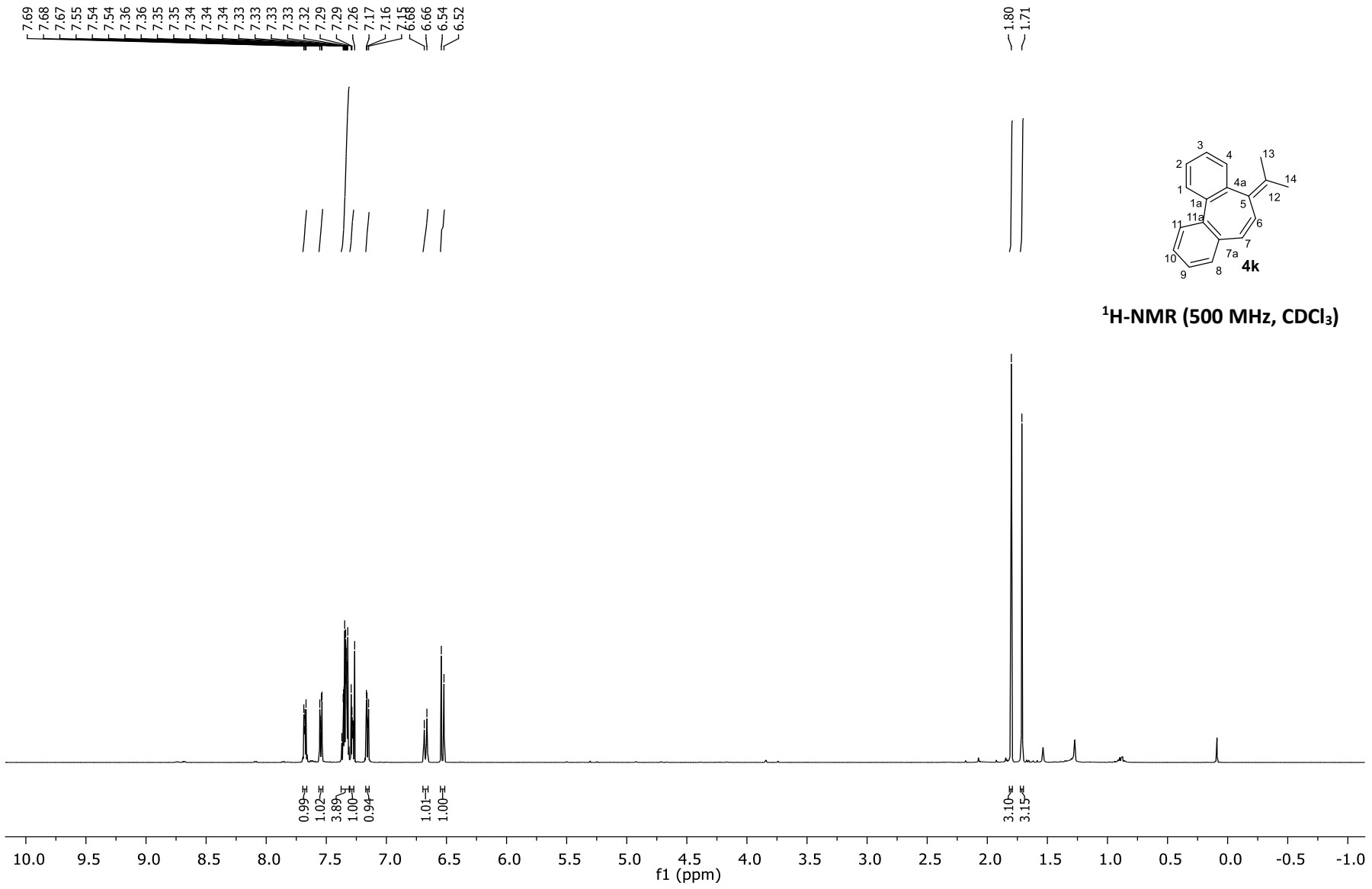
^{13}C-NMR (75 MHz, $CDCl_3$)



^{1}H-NMR (300 MHz, $CDCl_3$)

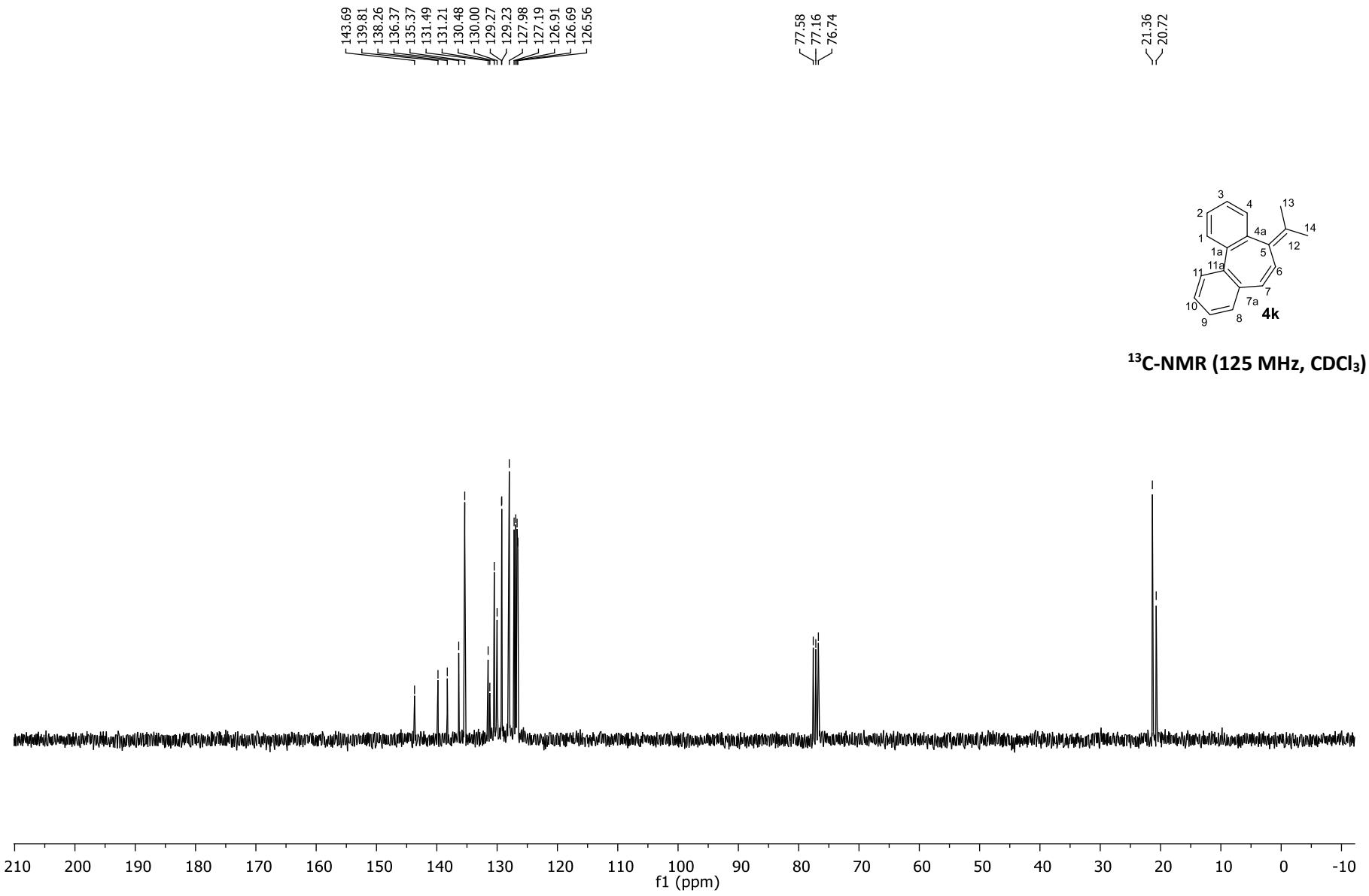


^{13}C-NMR (75 MHz, $CDCl_3$)



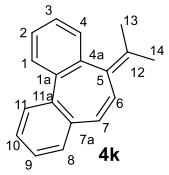
4k

^{1}H-NMR (500 MHz, $CDCl_3$)



4k

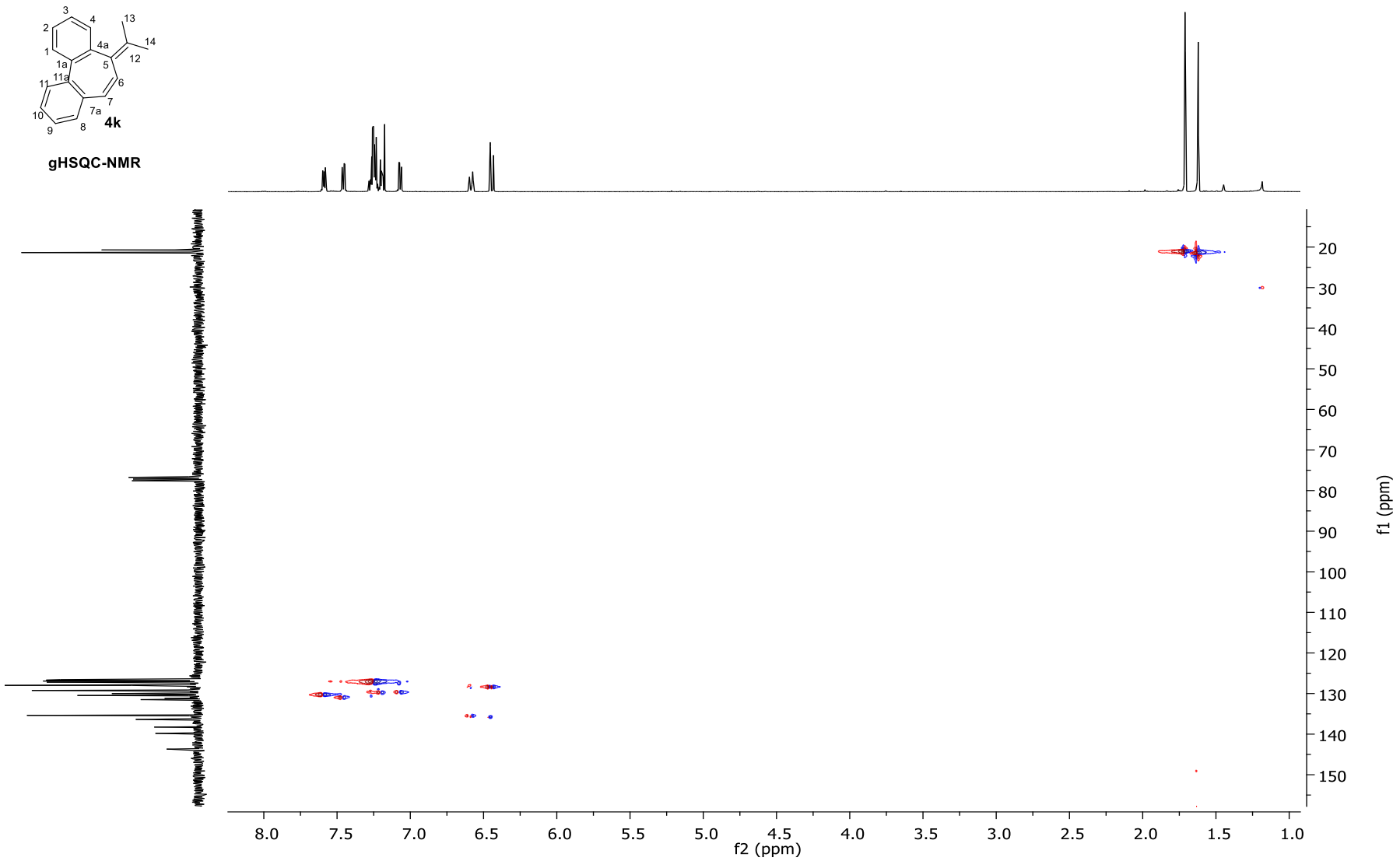
^{13}C-NMR (125 MHz, $CDCl_3$)

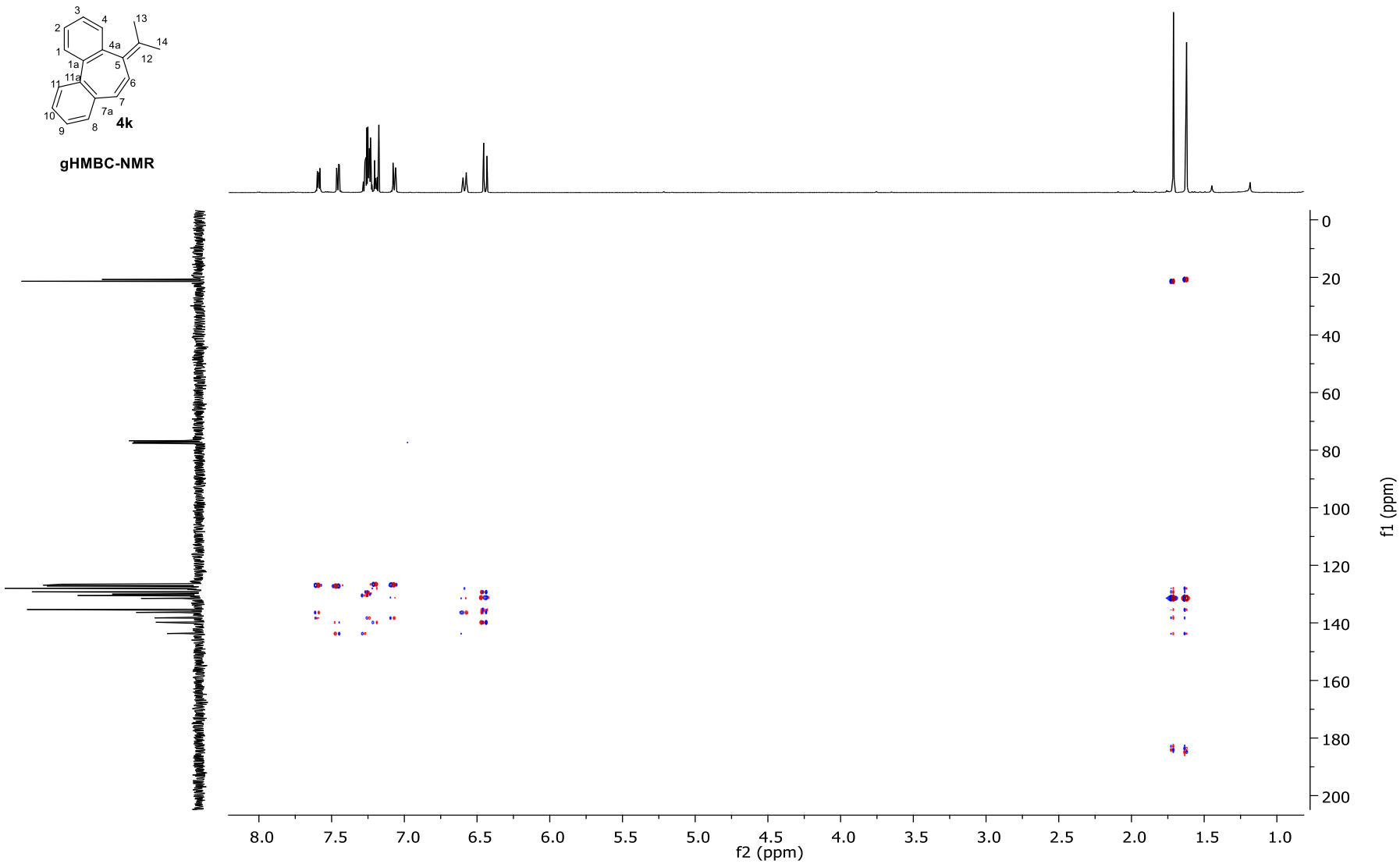

3
4
13
2
14
4a
1
12
1a
5
11
6
11a
7
7a
10
9
8

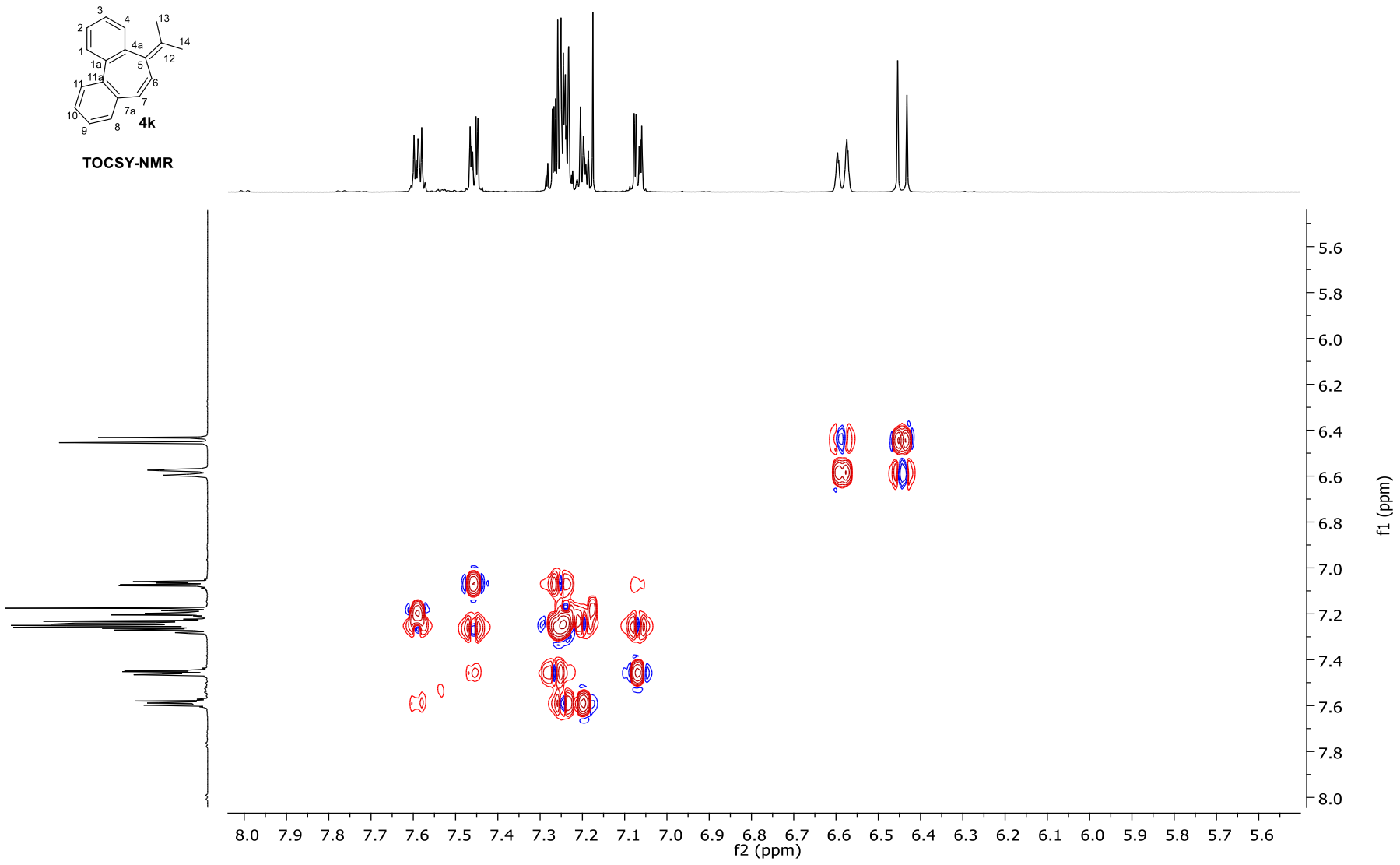
4k

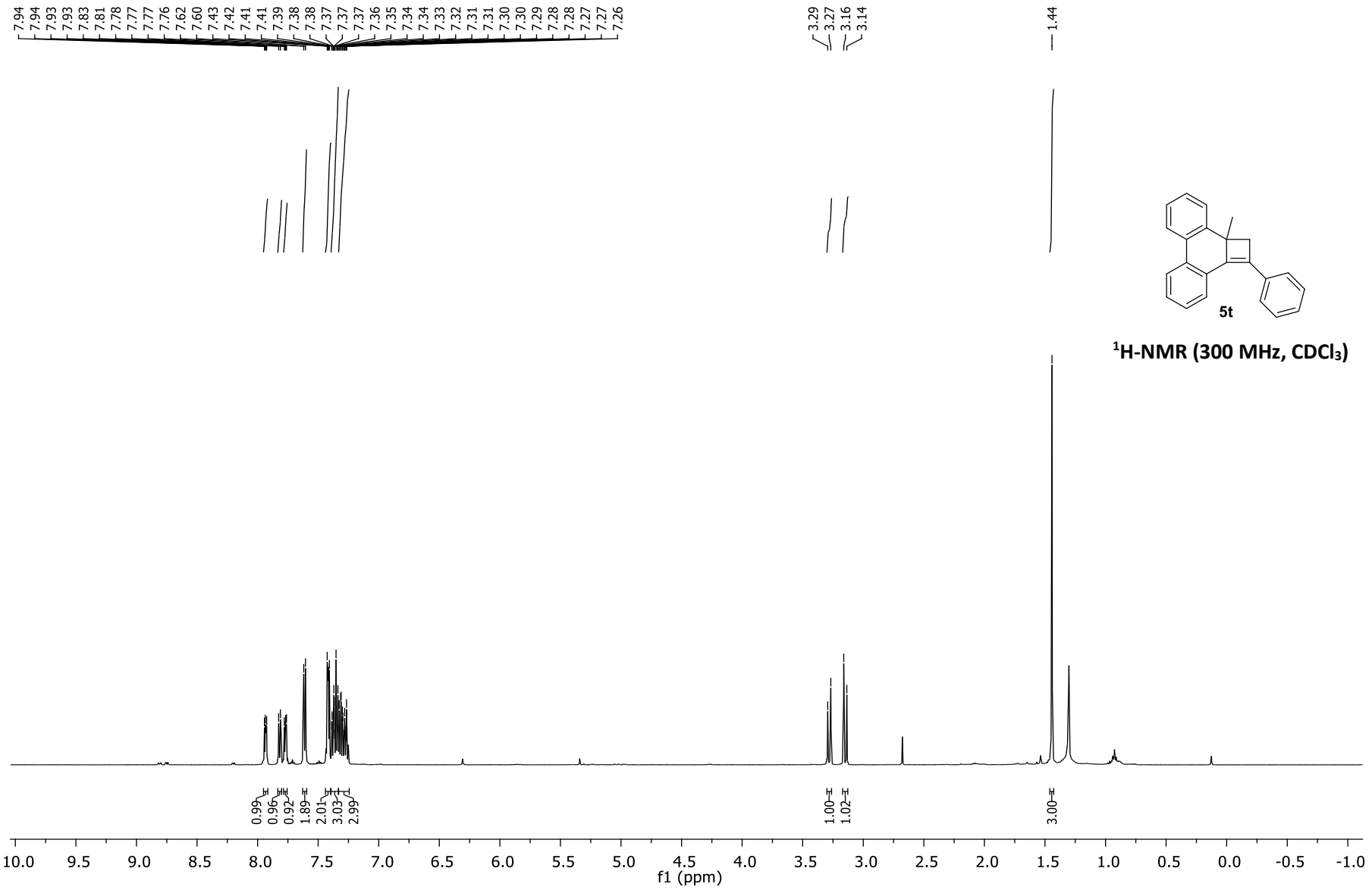
gCOSY-NMR

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)


4k
gHSQC-NMR
f2 (ppm)
f1 (ppm)

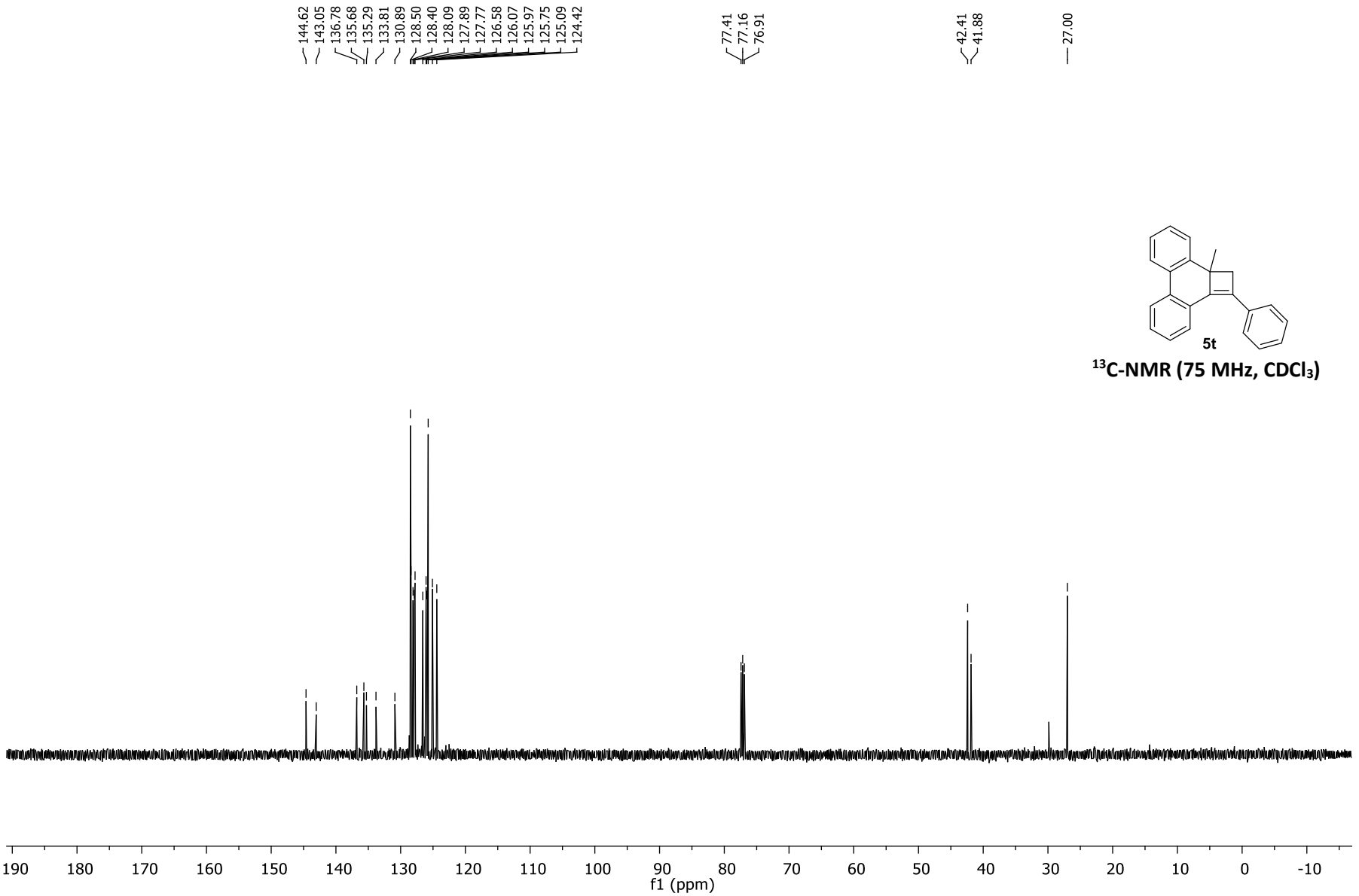

4k
gHMBC-NMR
f2 (ppm)
f1 (ppm)


4k
TOCSY-NMR
f2 (ppm)
f1 (ppm)

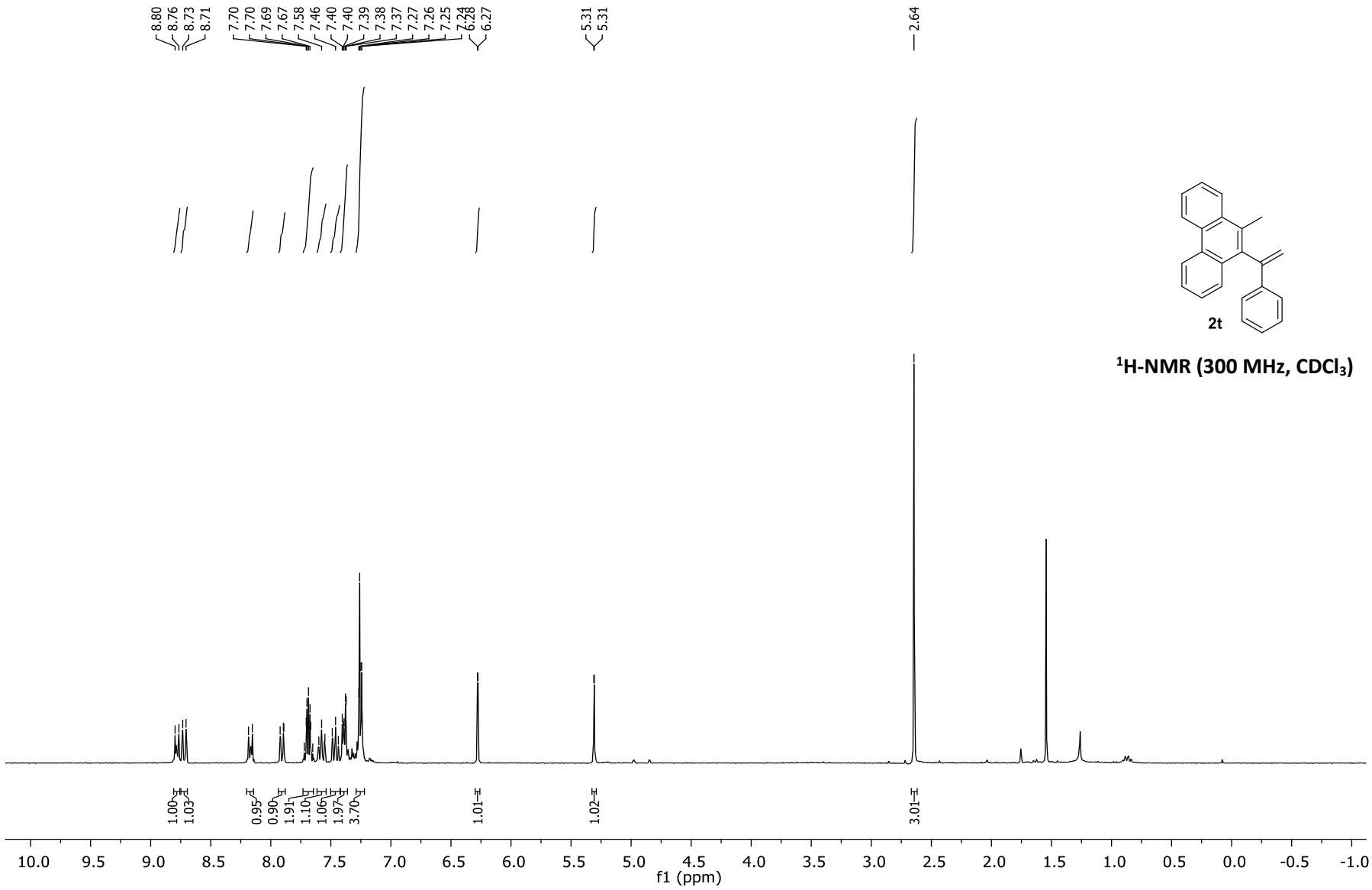


5t

^{1}H-NMR (300 MHz, $CDCl_3$)

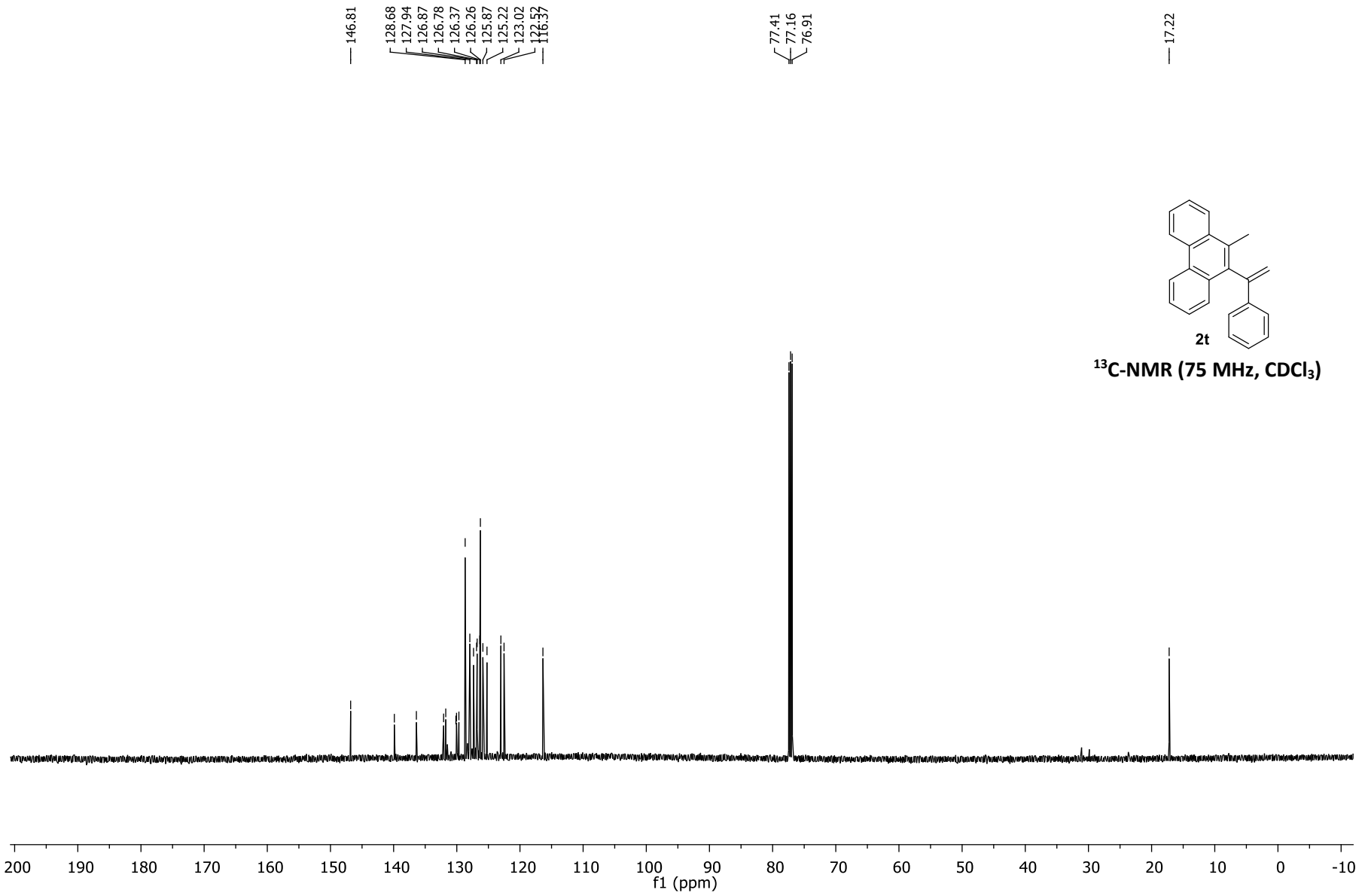


^{13}C-NMR (75 MHz, $CDCl_3$)

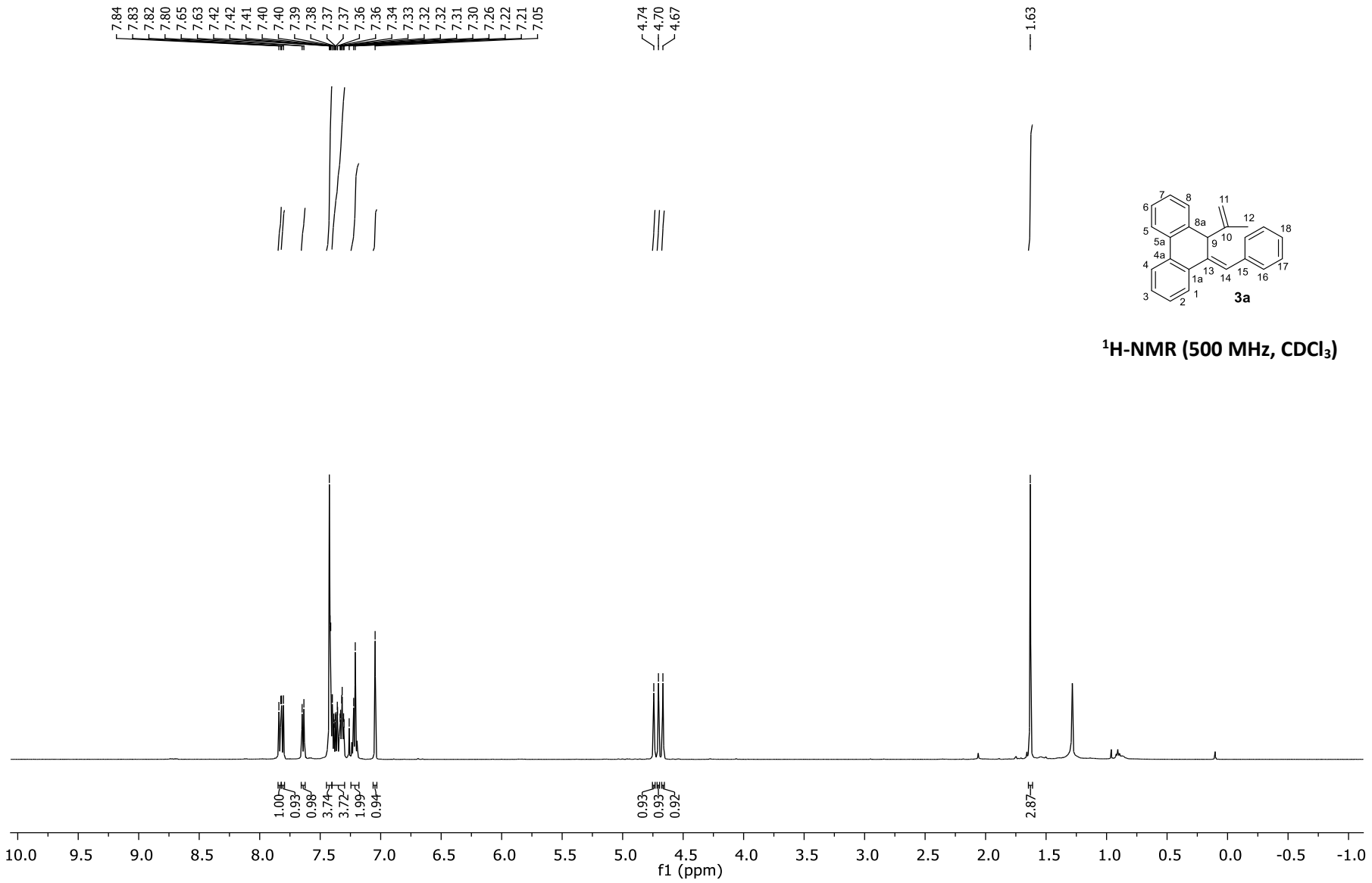


2t

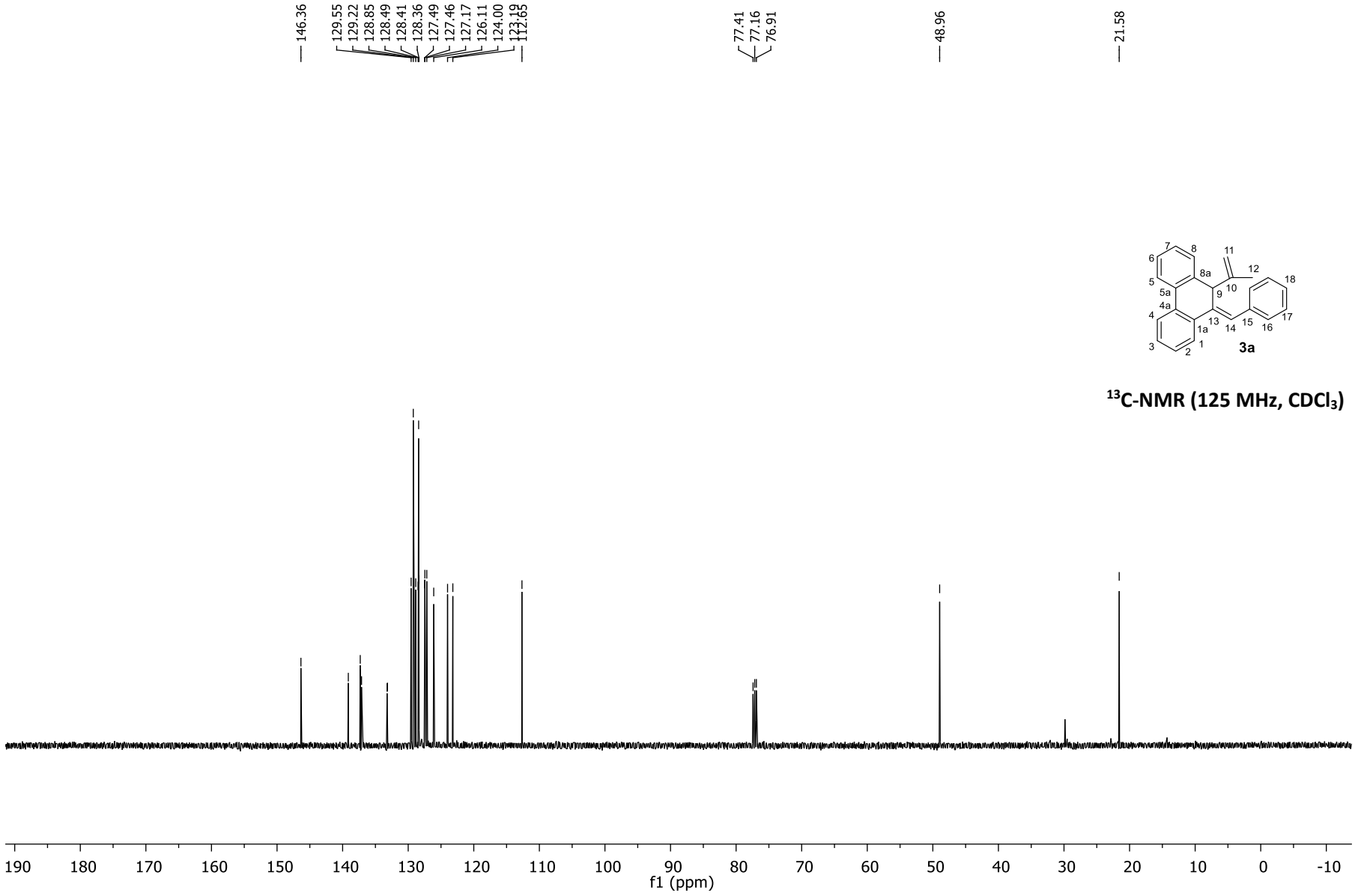
^{1}H-NMR (300 MHz, $CDCl_3$)



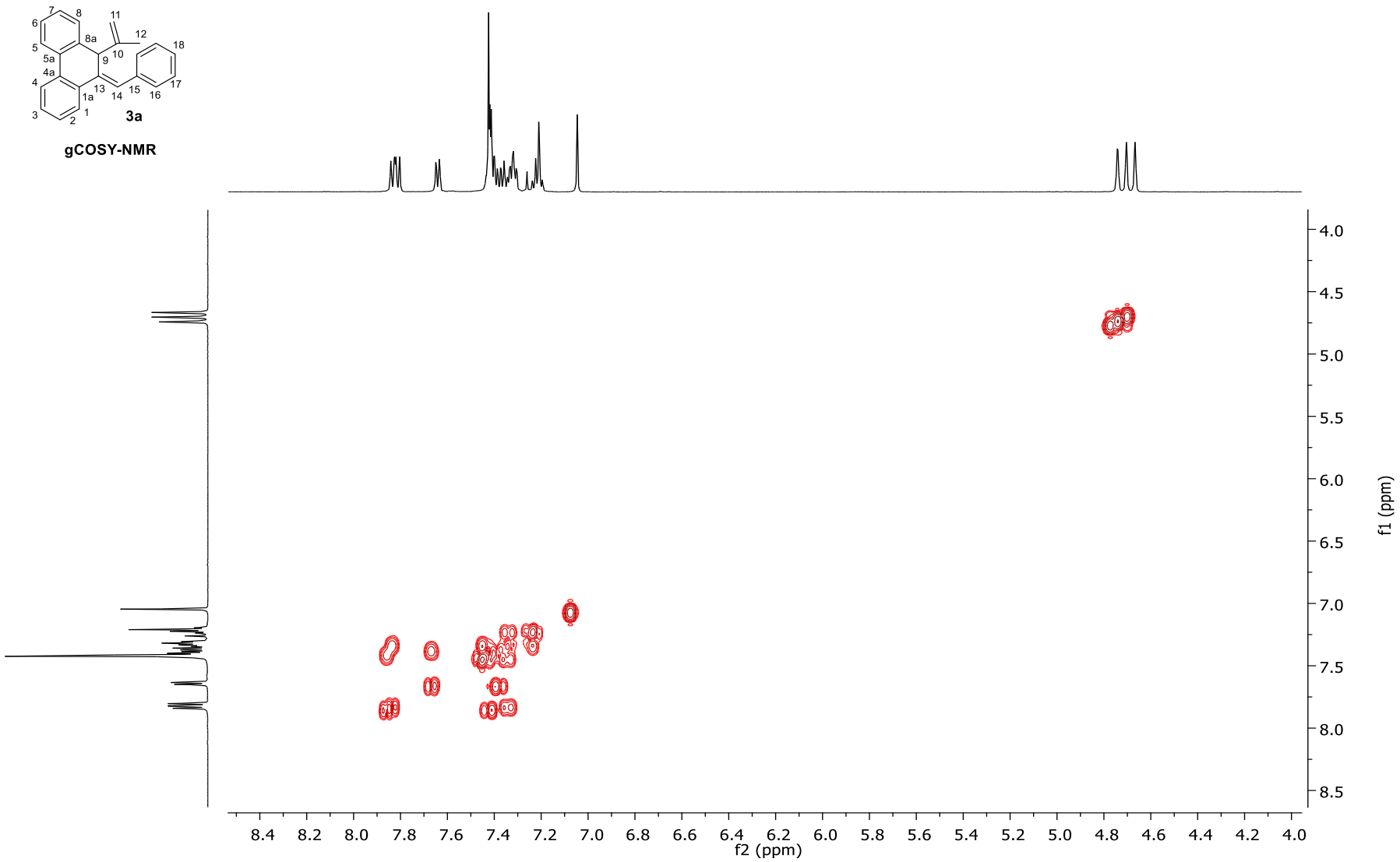
^{13}C-NMR (75 MHz, $CDCl_3$)

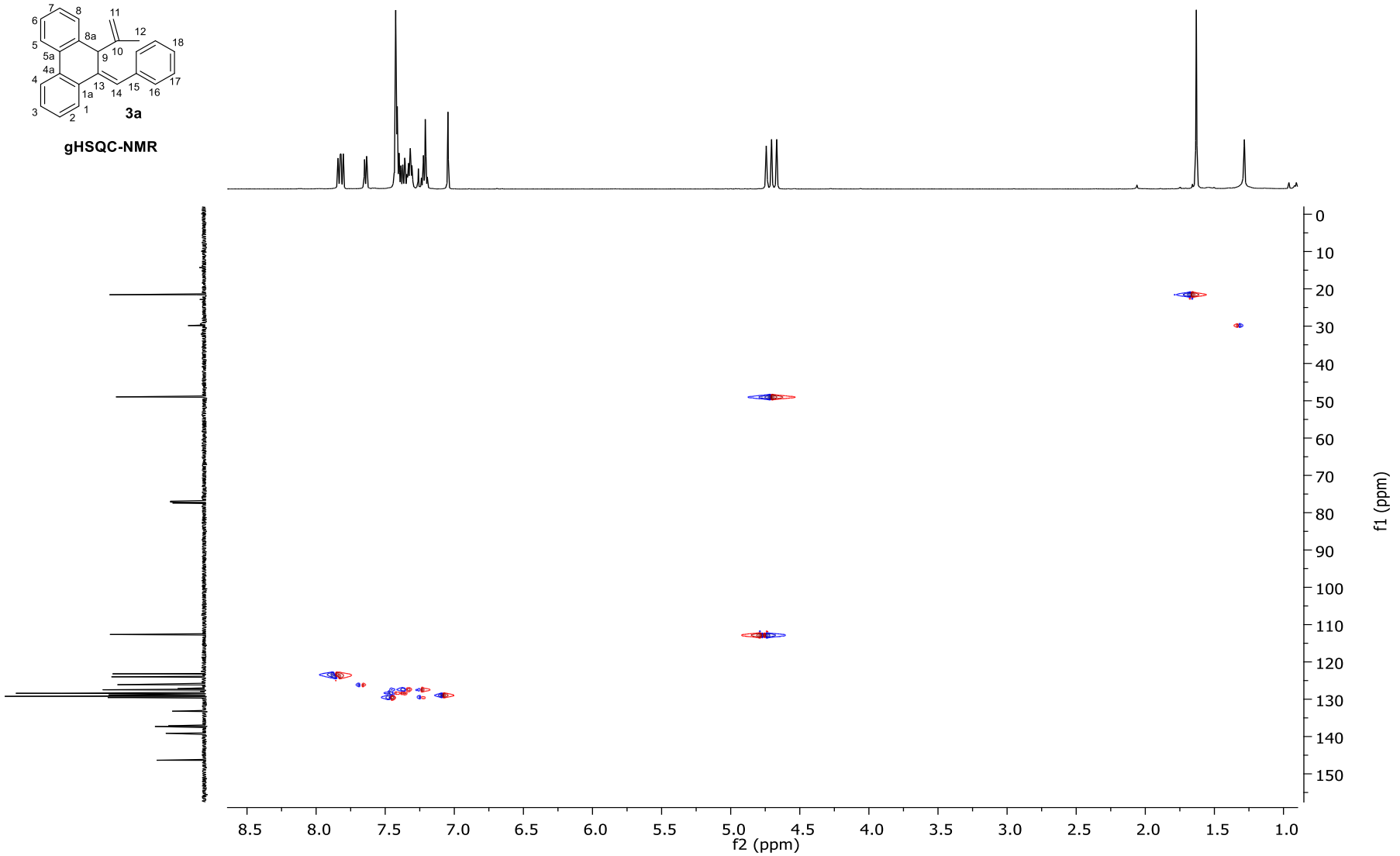


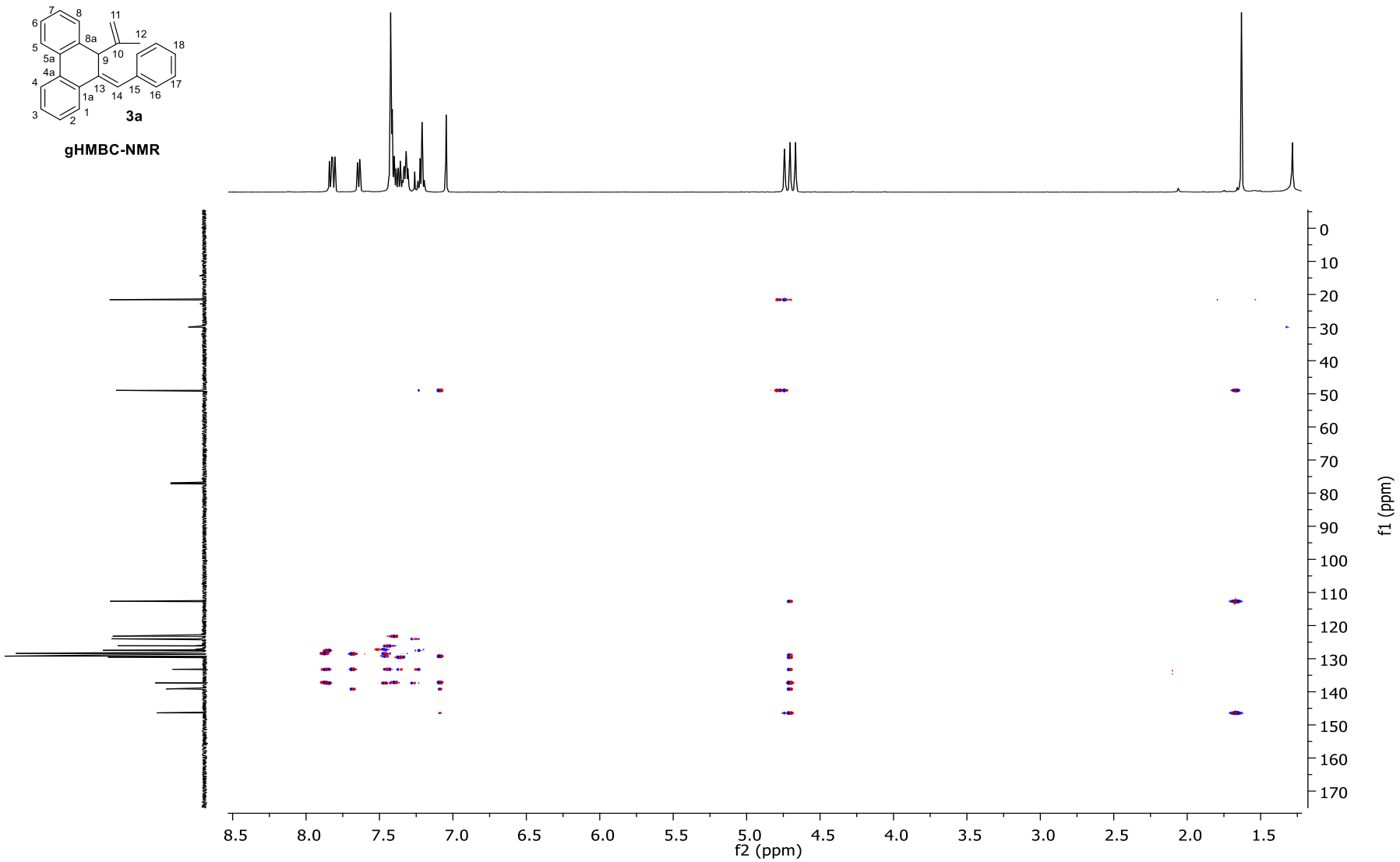
^{1}H-NMR (500 MHz, $CDCl_3$)

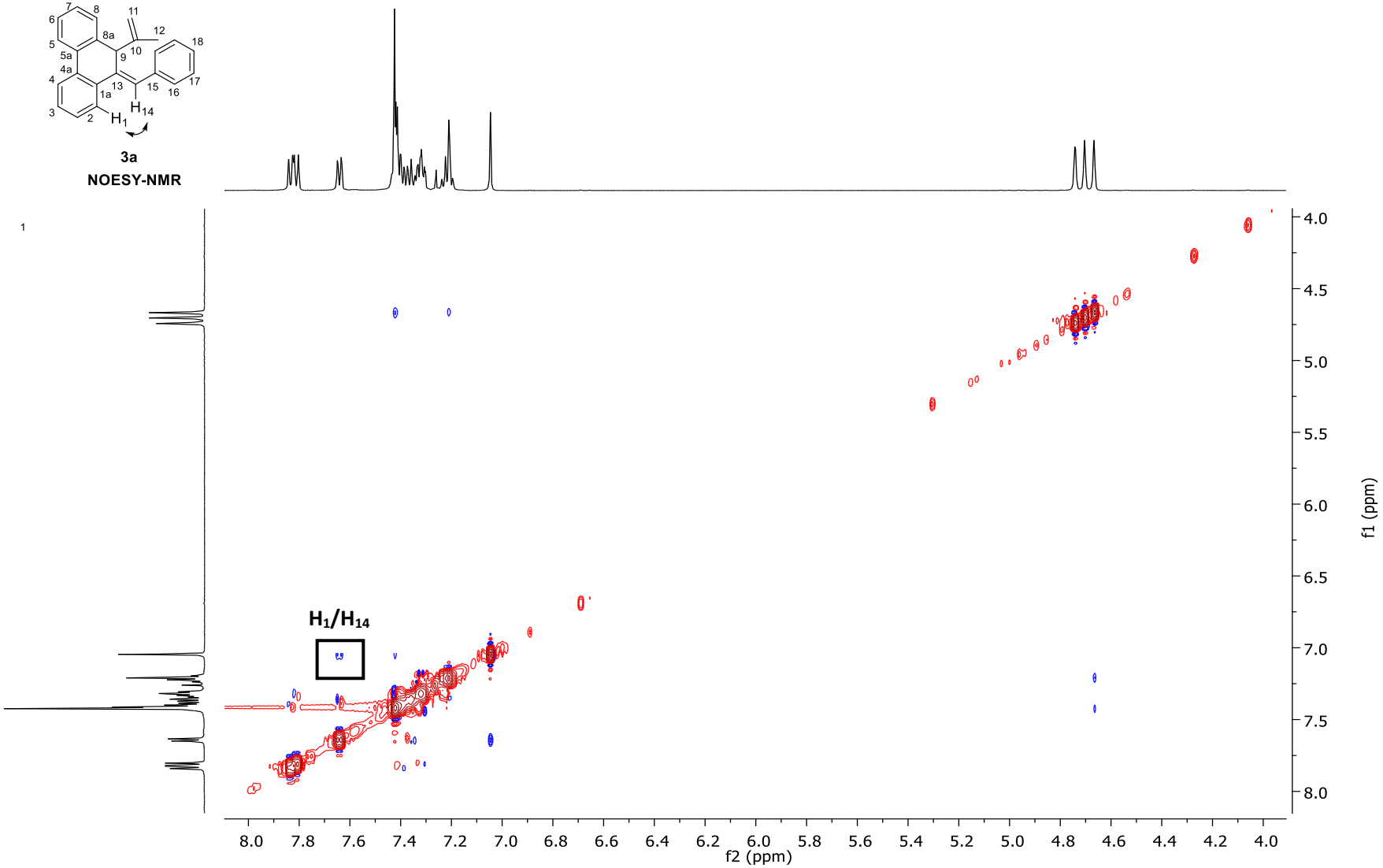


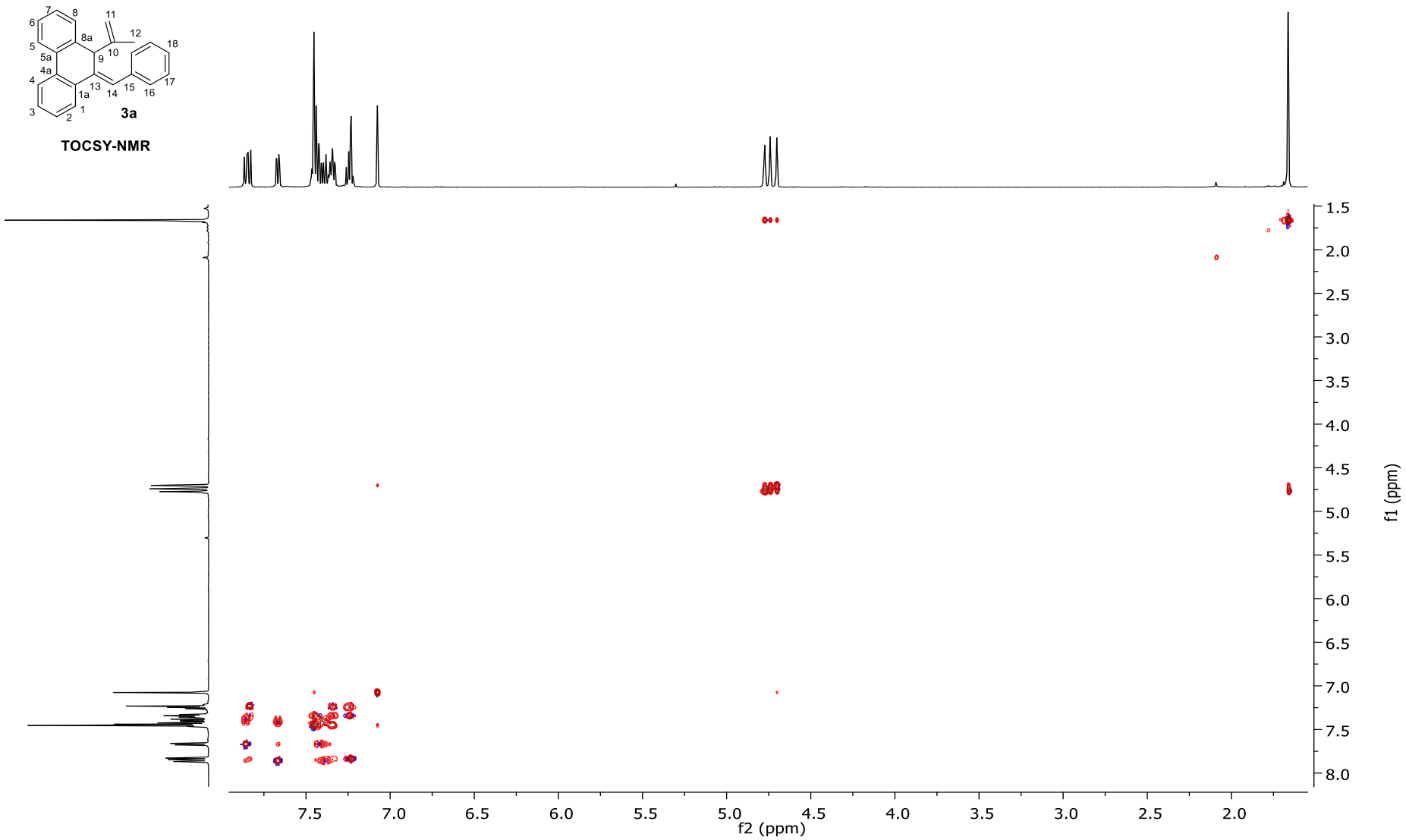
^{13}C-NMR (125 MHz, $CDCl_3$)

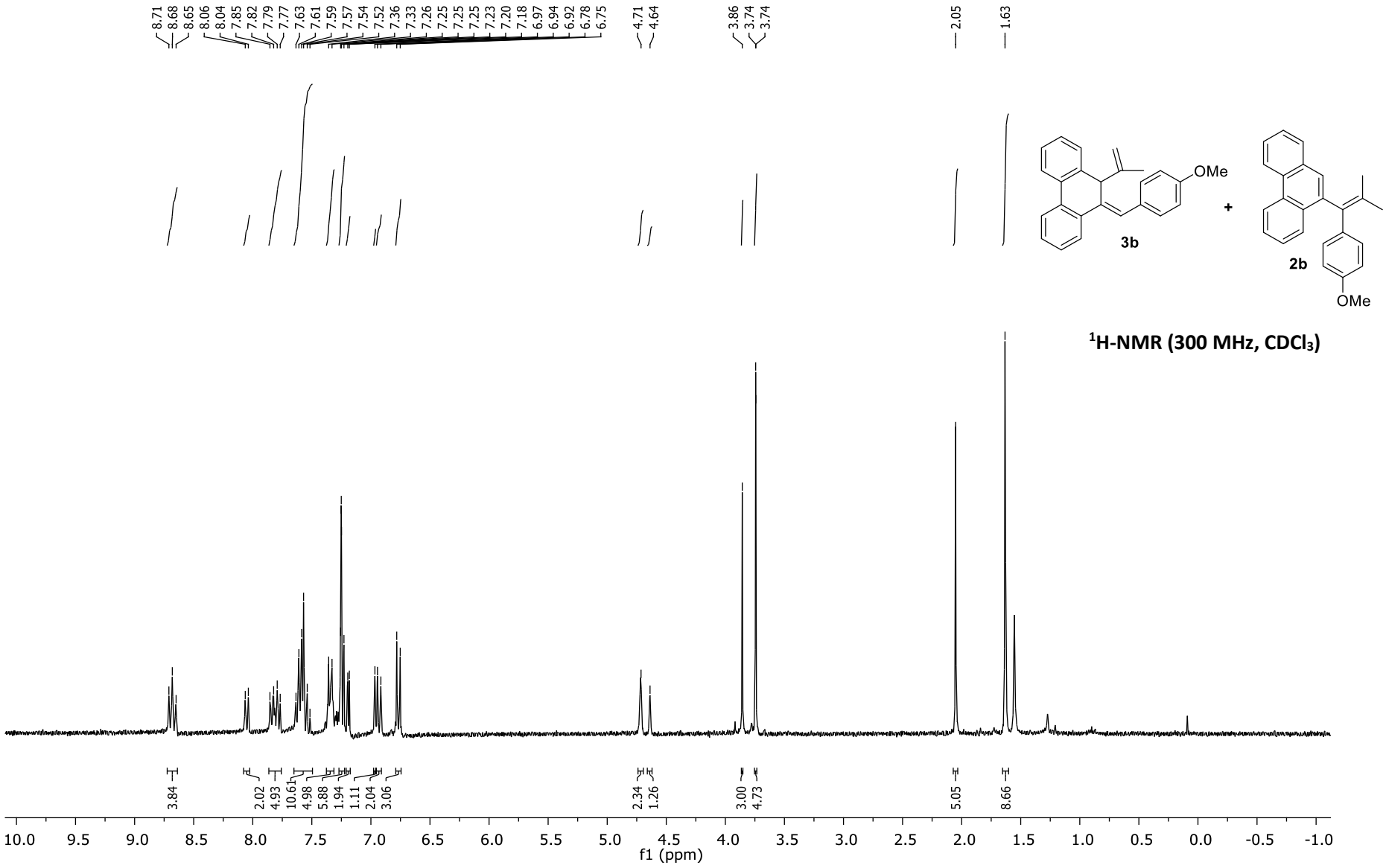

3a
gCOSY-NMR
f2 (ppm)
f1 (ppm)

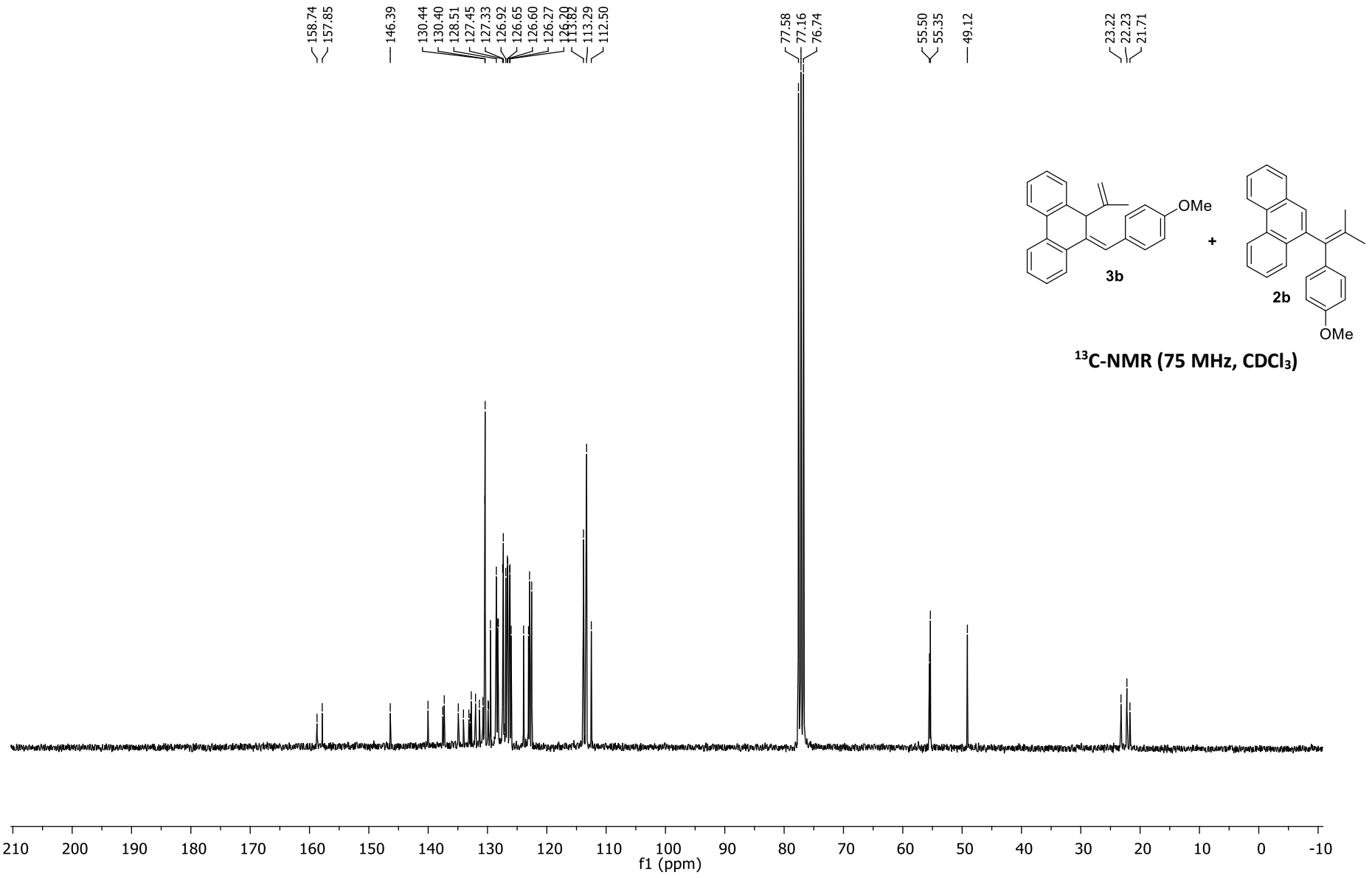

3a
gHSQC-NMR
f2 (ppm)
f1 (ppm)


3a
gHMBC-NMR
f2 (ppm)
f1 (ppm)

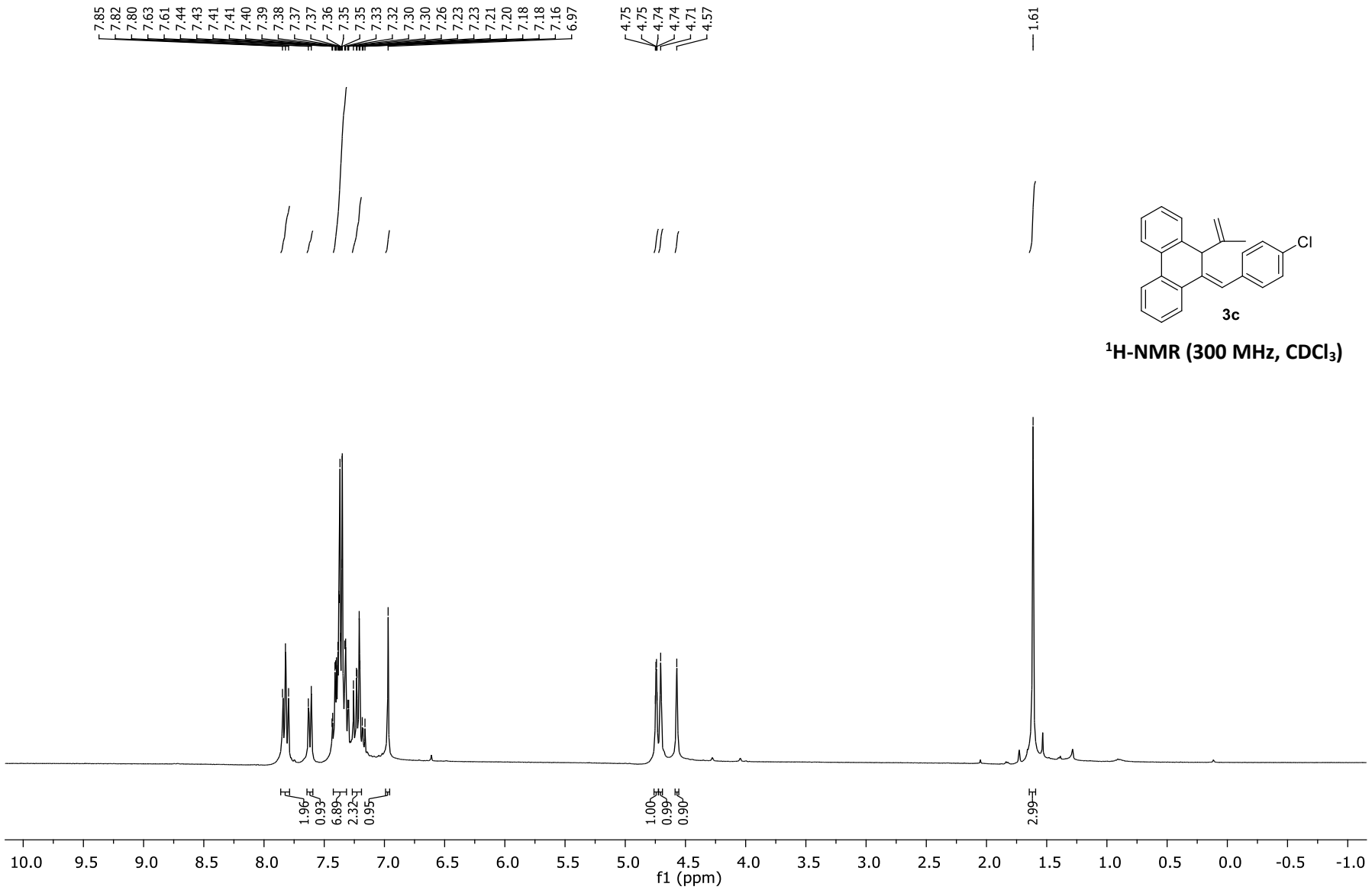

3a
NOESY-NMR
H1/H14
f2 (ppm)
f1 (ppm)


3a
TOCSY-NMR
f2 (ppm)
f1 (ppm)

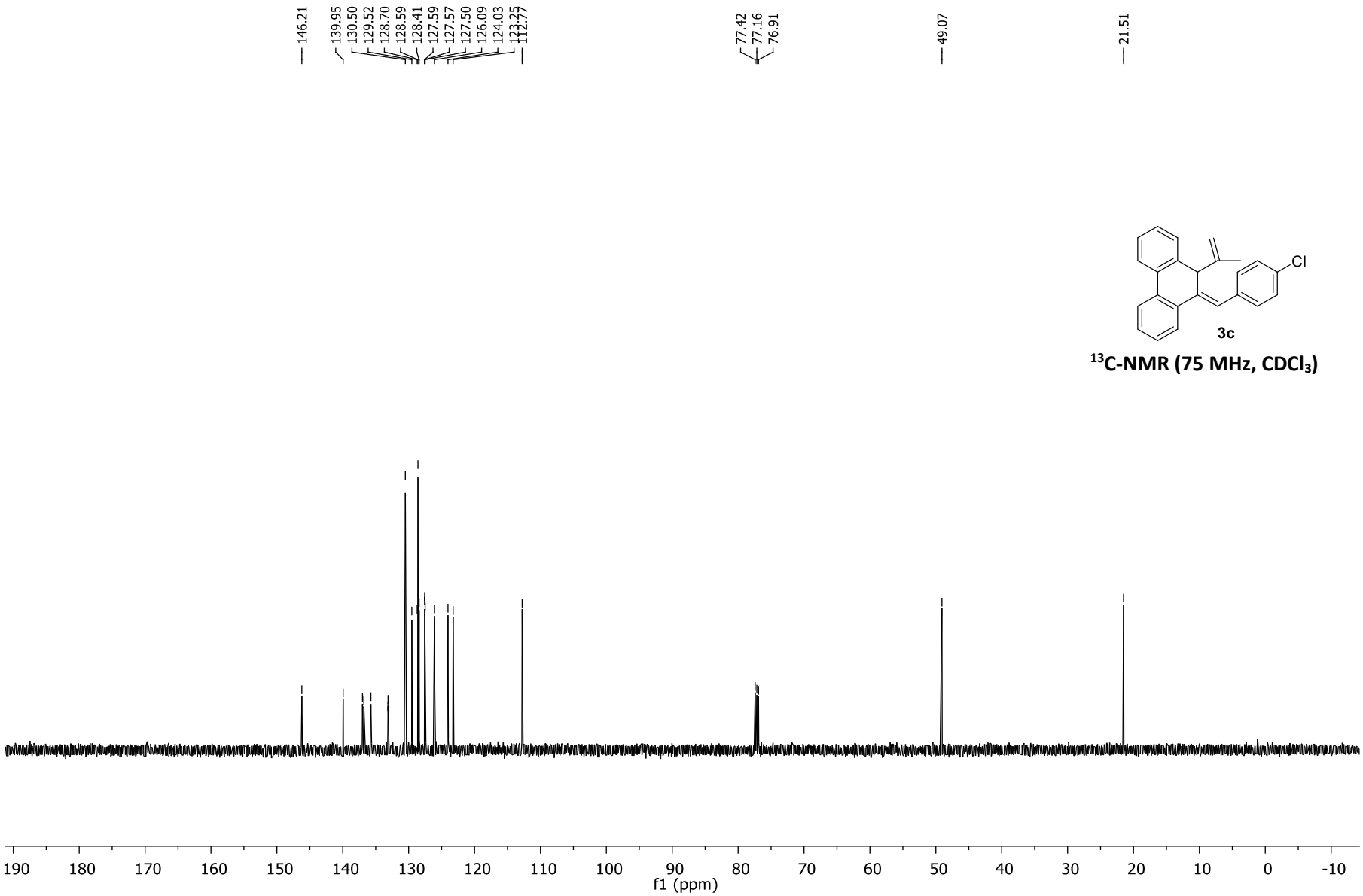

8.71
8.68
8.65
8.06
8.04
7.85
7.82
7.79
7.77
7.63
7.61
7.59
7.57
7.54
7.52
7.36
7.33
7.26
7.25
7.25
7.25
7.23
7.20
7.18
6.97
6.94
6.92
6.78
6.75
4.71
4.64
3.86
3.74
3.74
2.05
1.63
OMe
3b
+
2b
OMe
1H-NMR (300 MHz, CDCl3)
3.84
2.02
4.93
10.61
4.98
5.88
1.94
1.11
2.04
3.06
2.34
1.26
3.00
4.73
5.05
8.66
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

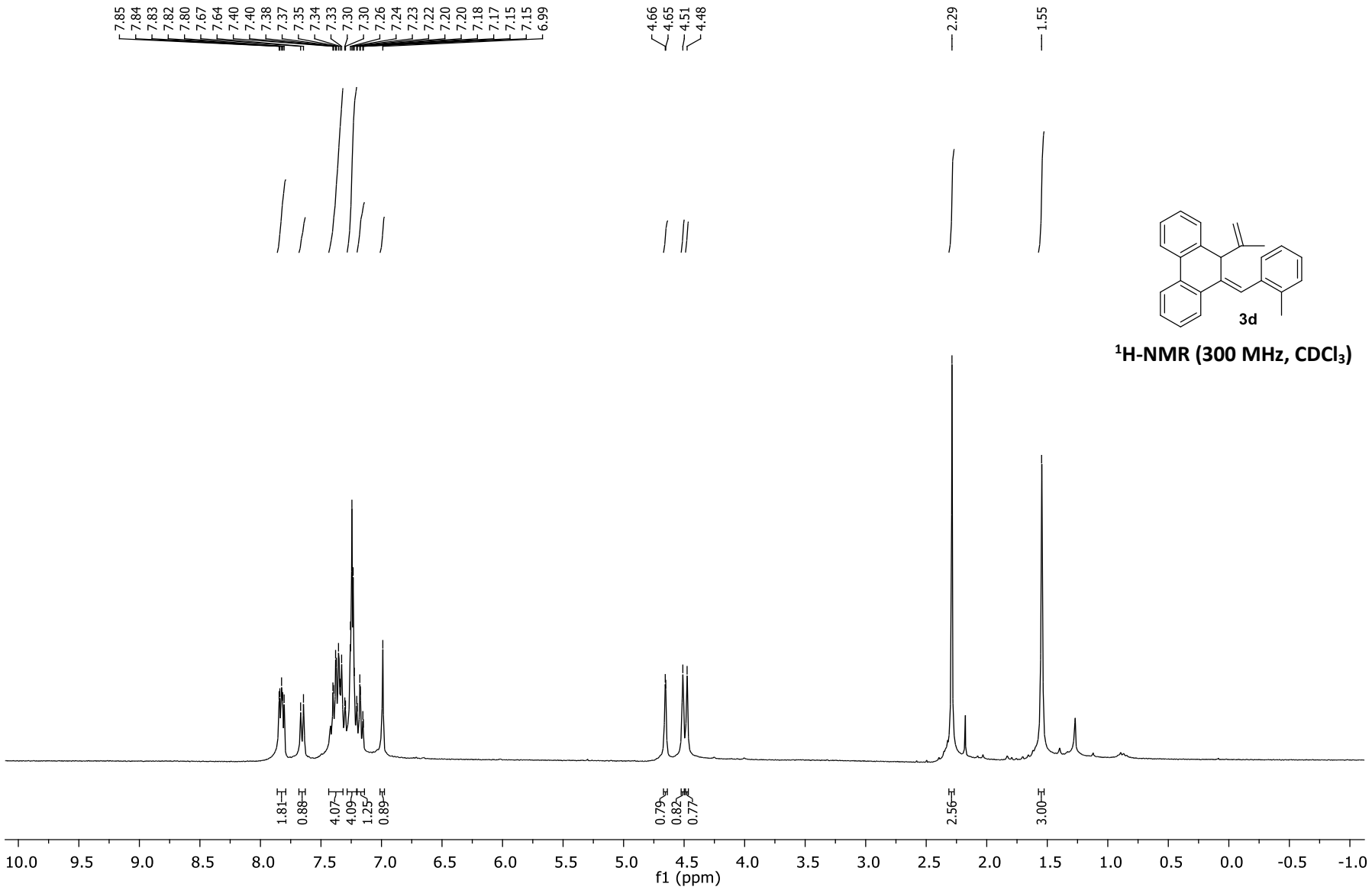


^{13}C-NMR (75 MHz, $CDCl_3$)



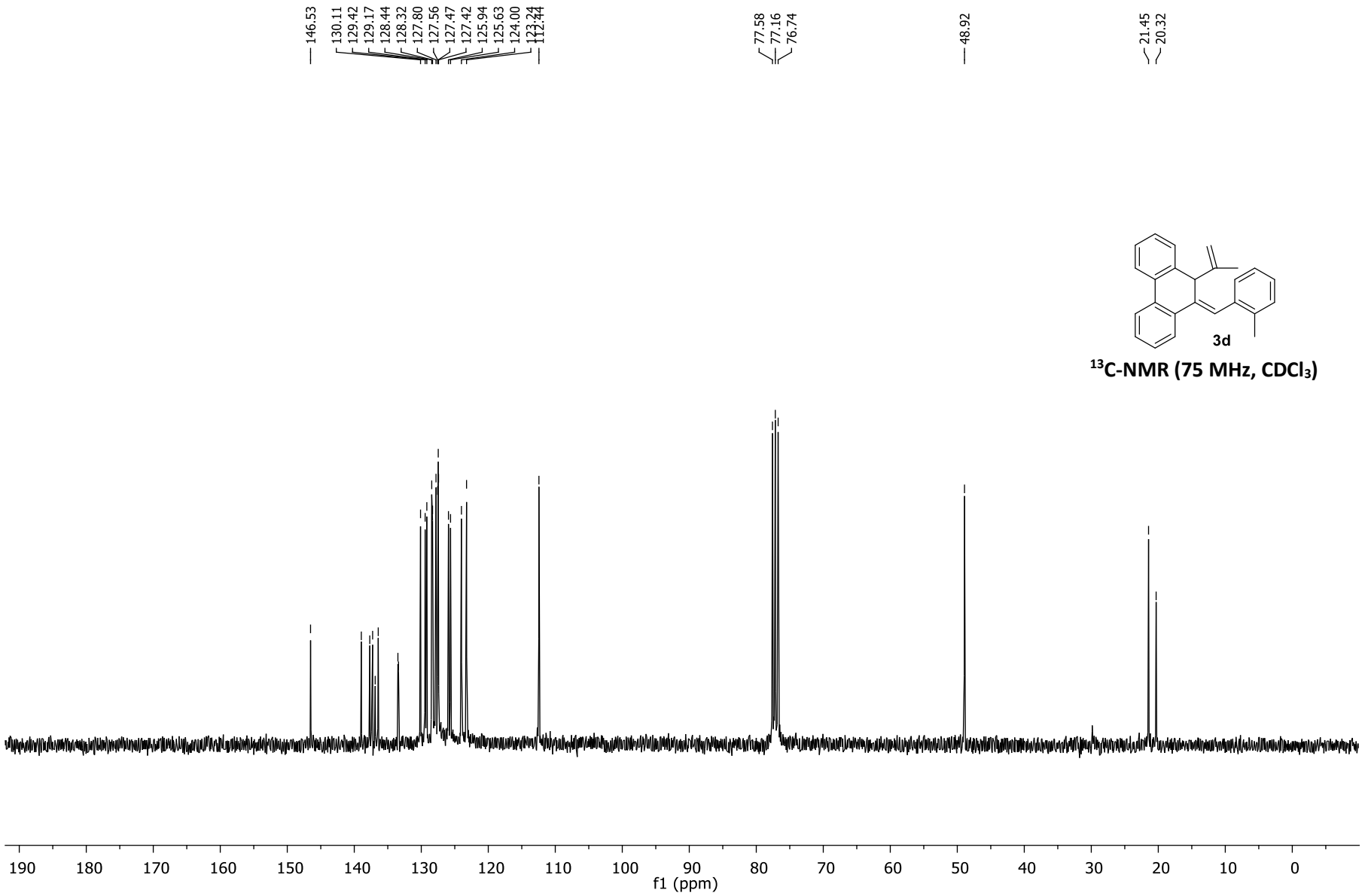
^{1}H-NMR (300 MHz, $CDCl_3$)

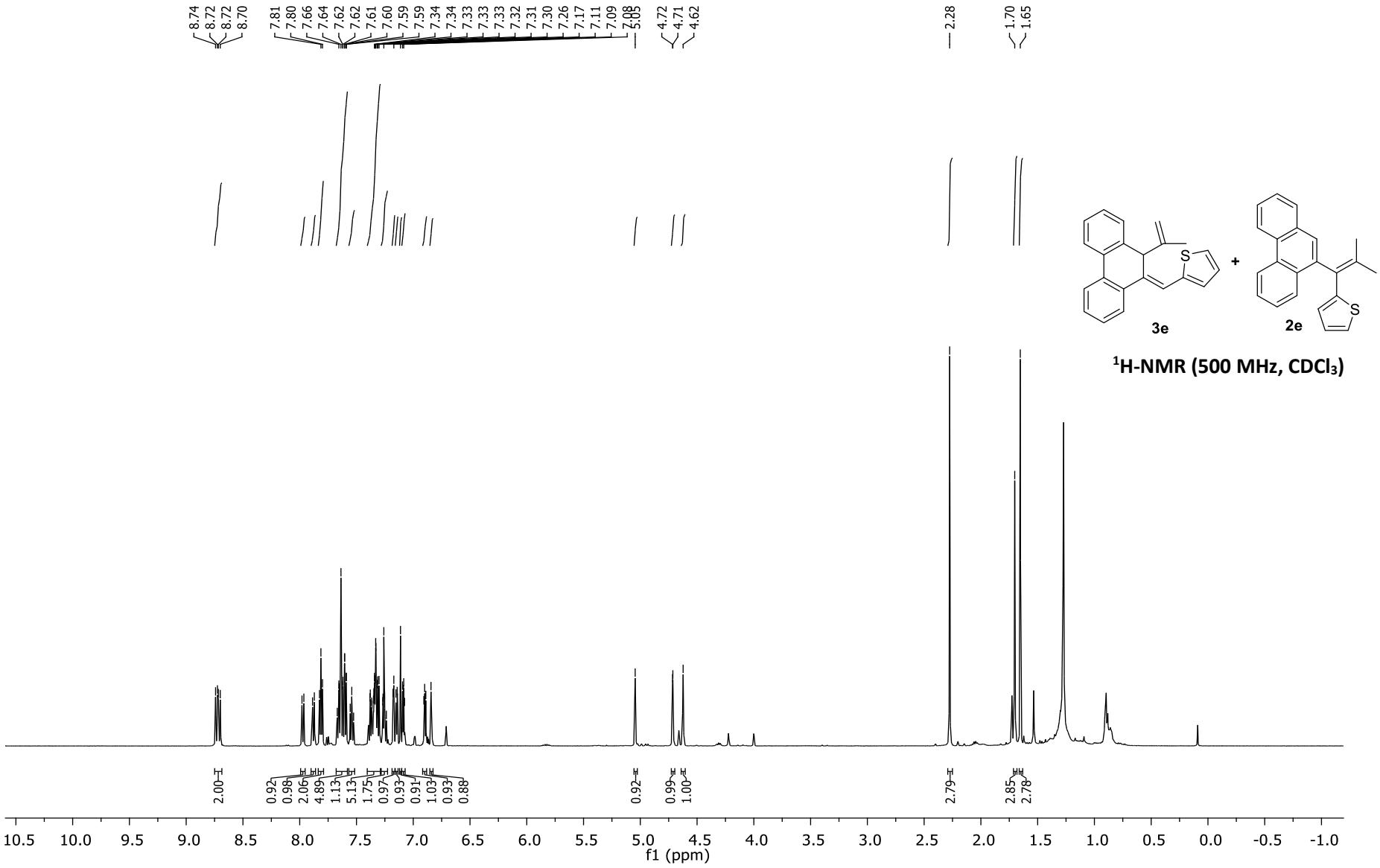

146.21
139.95
130.50
129.52
128.70
128.59
128.41
127.59
127.57
127.50
126.09
124.03
123.25
112.77
77.42
77.16
76.91
49.07
21.51
Cl
3c
^{13}C-NMR (75 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

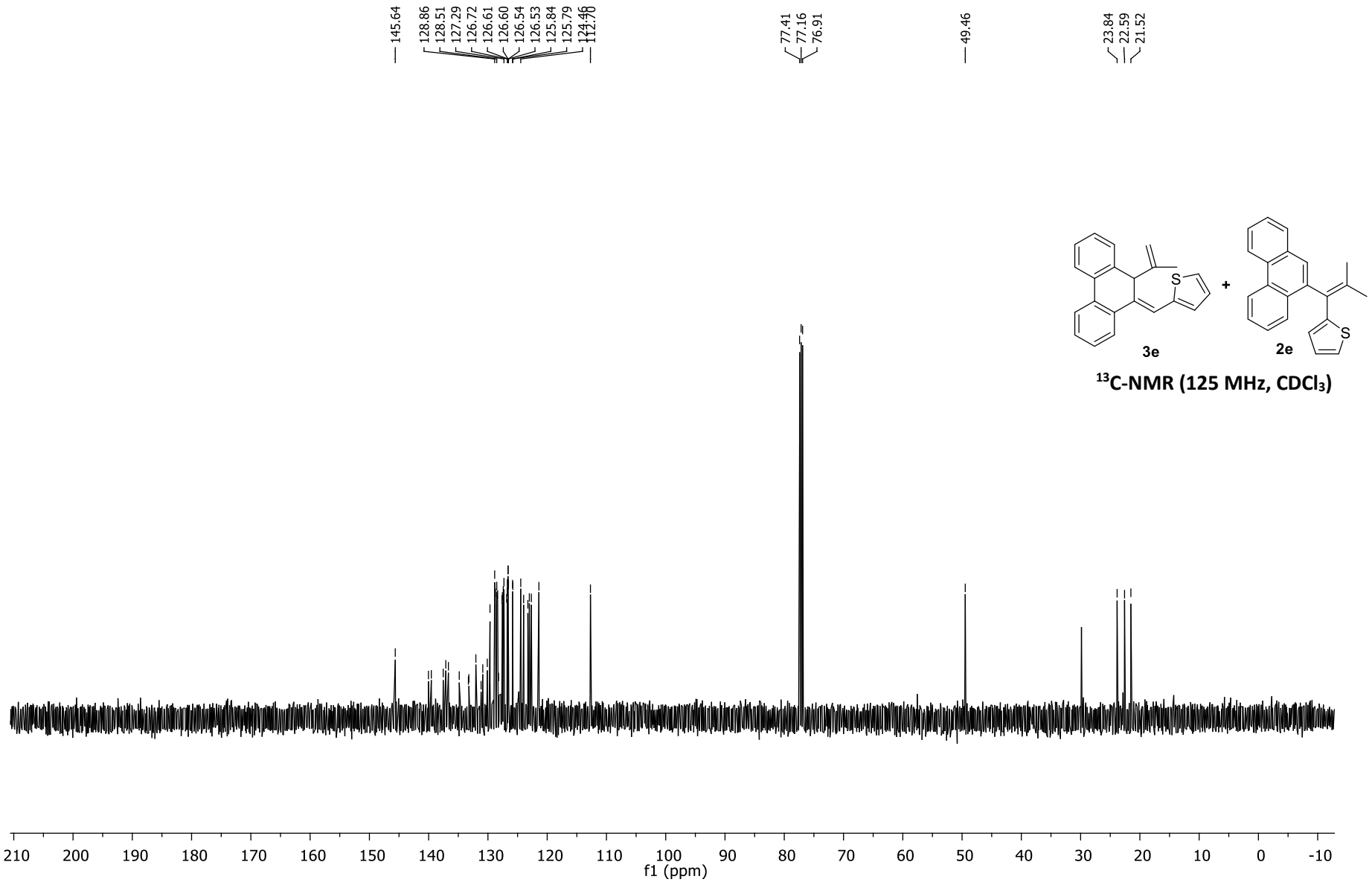


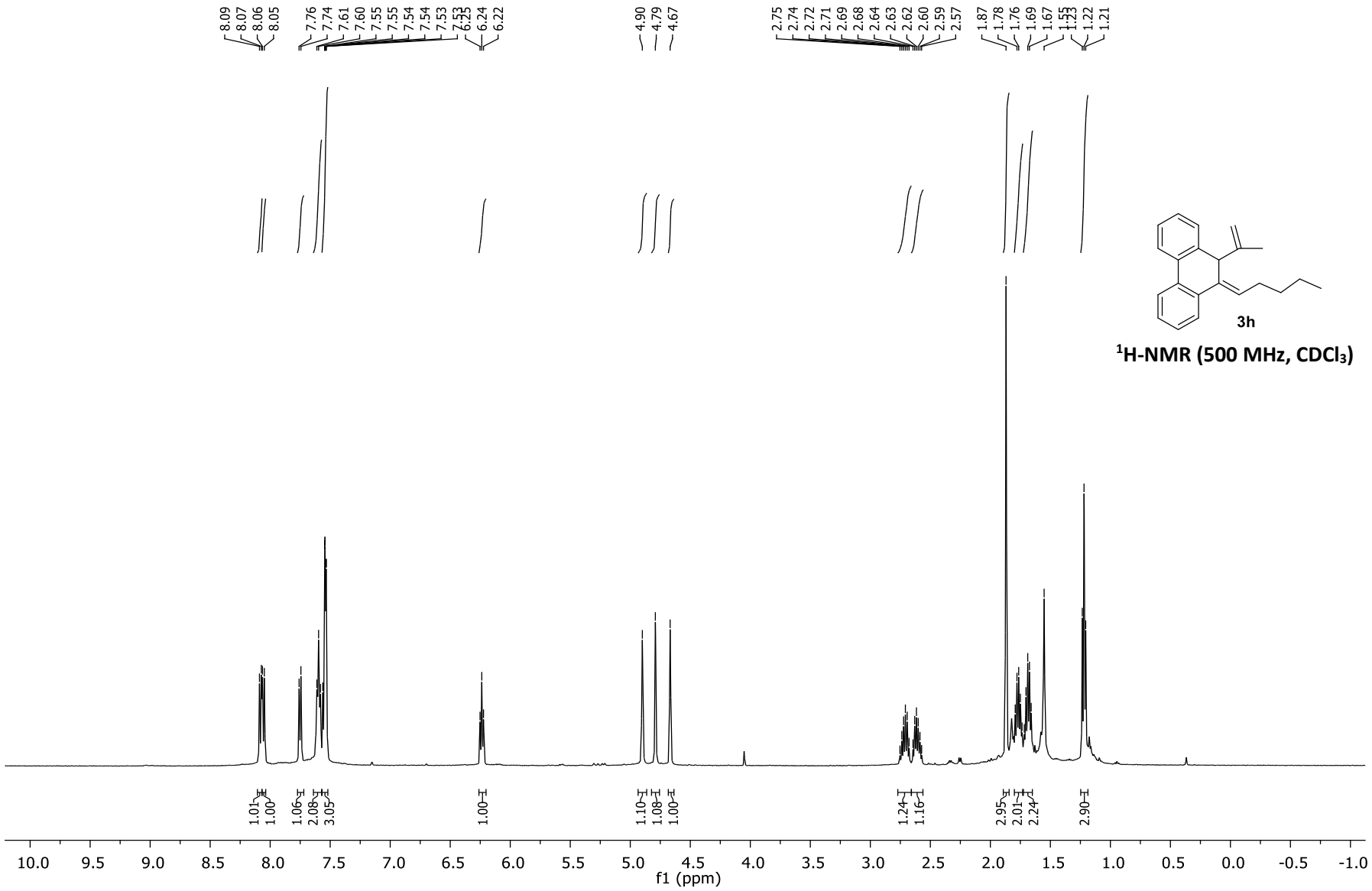
3d

^{1}H-NMR (300 MHz, $CDCl_3$)


146.53
130.11
129.42
129.17
128.44
128.32
127.80
127.56
127.47
127.42
125.94
125.63
124.00
123.24
112.44
77.58
77.16
76.74
48.92
21.45
20.32
3d
13C-NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

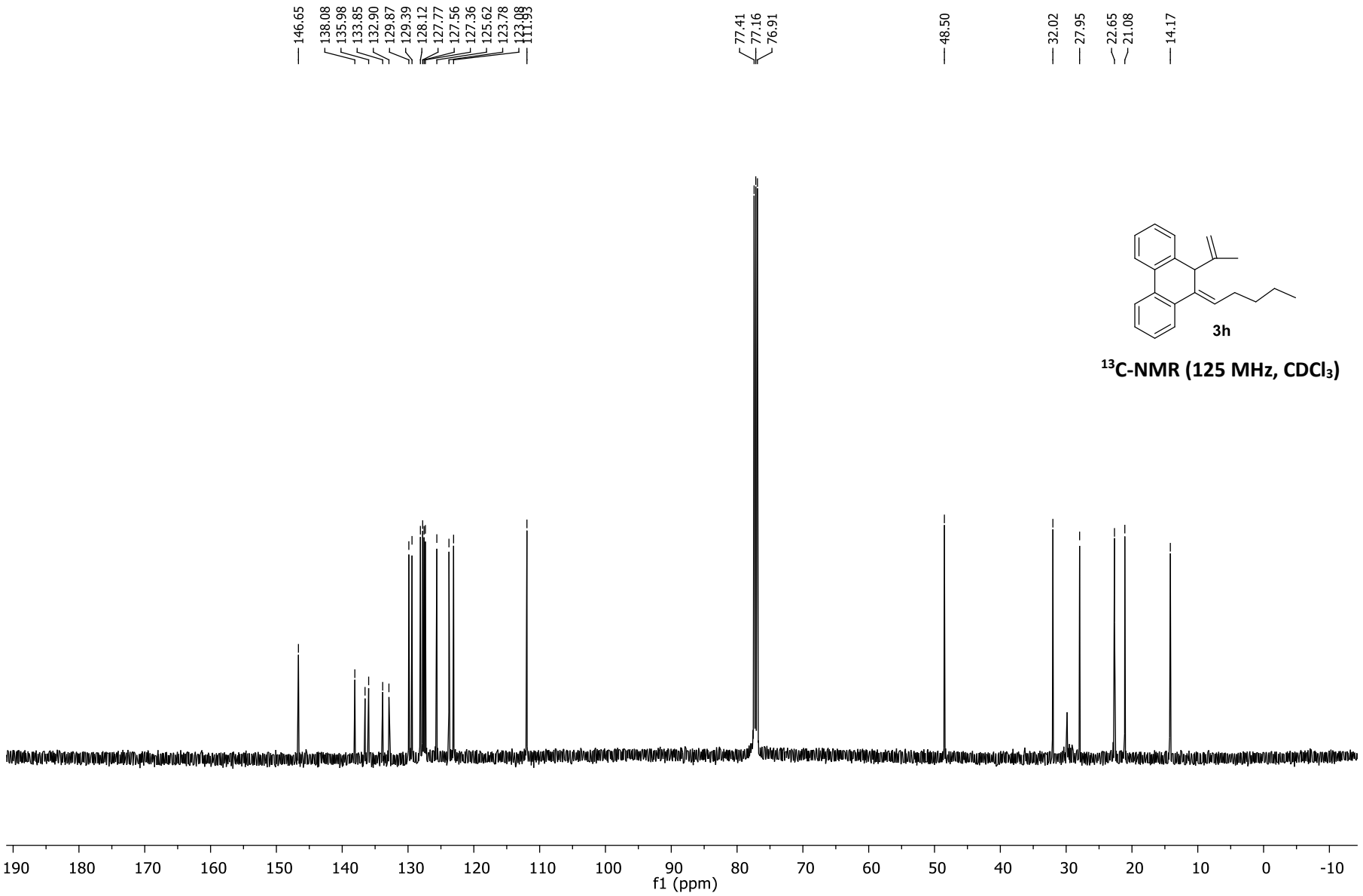

8.74
8.72
8.72
8.70
7.81
7.80
7.66
7.64
7.62
7.62
7.61
7.60
7.59
7.59
7.34
7.34
7.33
7.33
7.33
7.32
7.31
7.30
7.26
7.17
7.11
7.09
7.08
5.05
4.72
4.71
4.62
2.28
1.70
1.65
3e
+
2e
1H-NMR (500 MHz, CDCl3)
2.00
0.92
0.98
2.06
4.89
1.13
5.13
1.75
0.97
0.93
0.91
1.03
0.93
0.88
0.92
0.99
1.00
2.79
2.85
2.78
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


145.64
128.86
128.51
127.29
126.72
126.61
126.60
126.54
126.53
125.84
125.79
124.46
112.70
77.41
77.16
76.91
49.46
23.84
22.59
21.52
S
+
S
3e
2e
^{13}C-NMR (125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

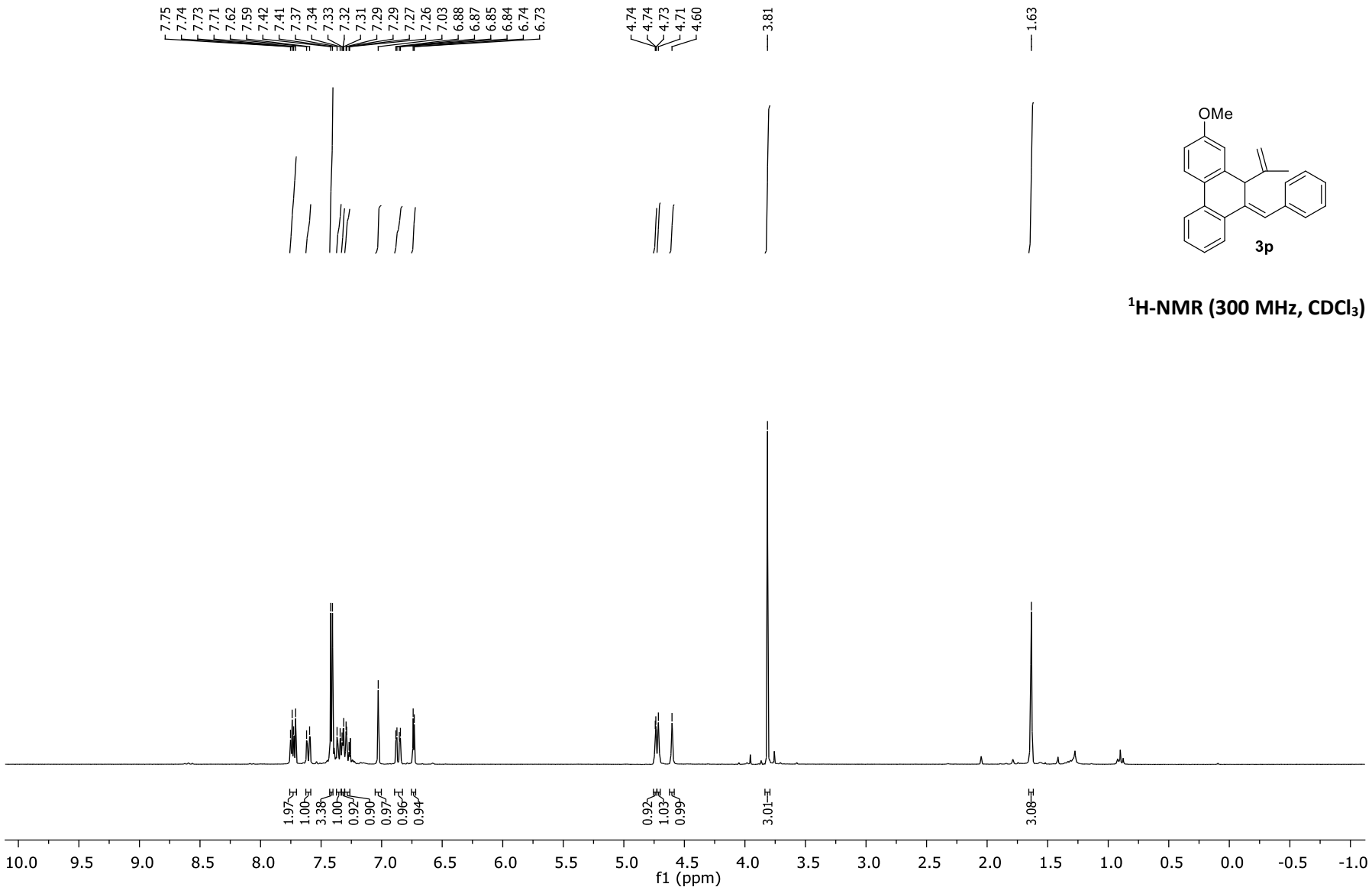


3h

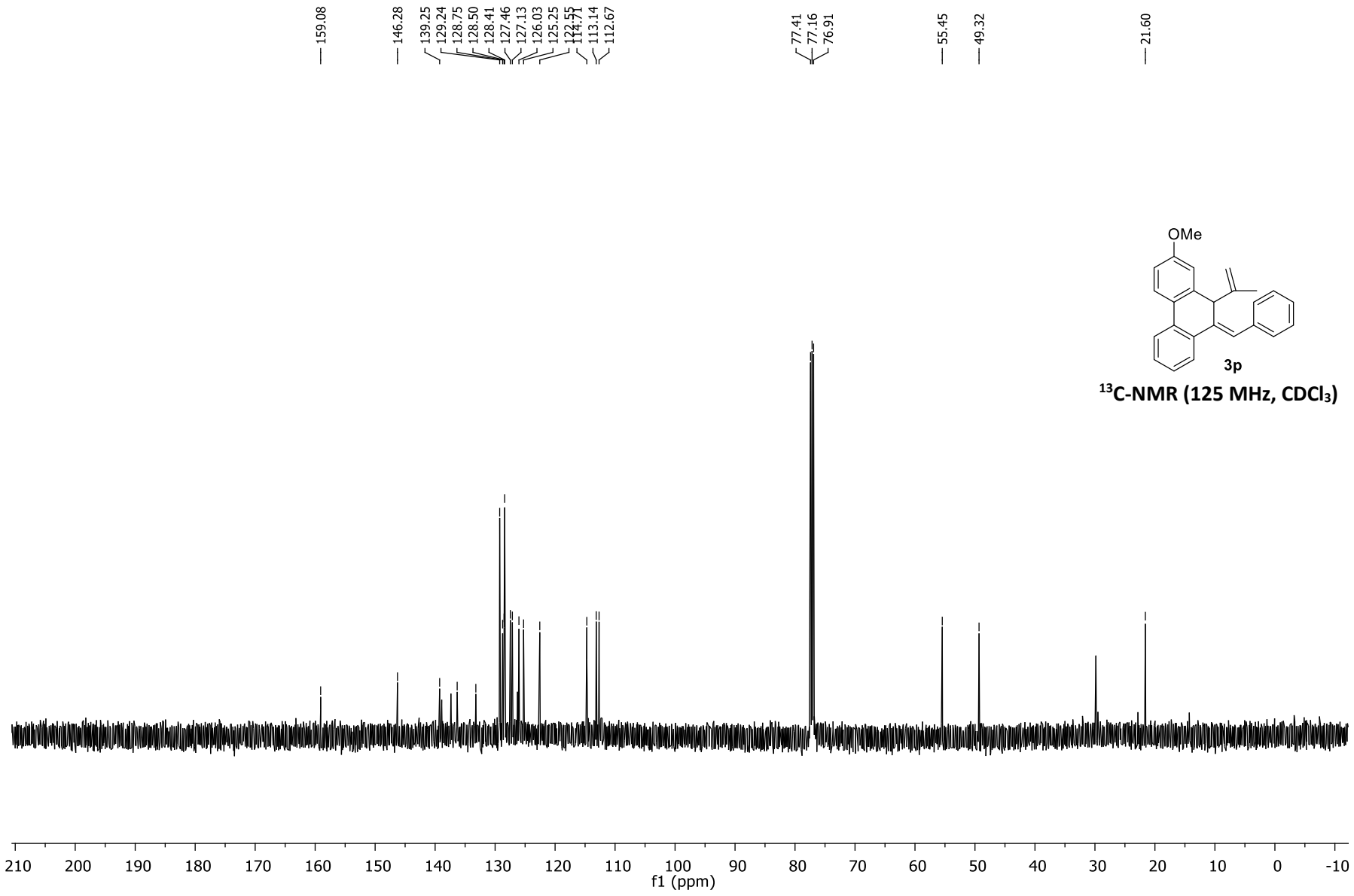
^{1}H-NMR (500 MHz, $CDCl_3$)

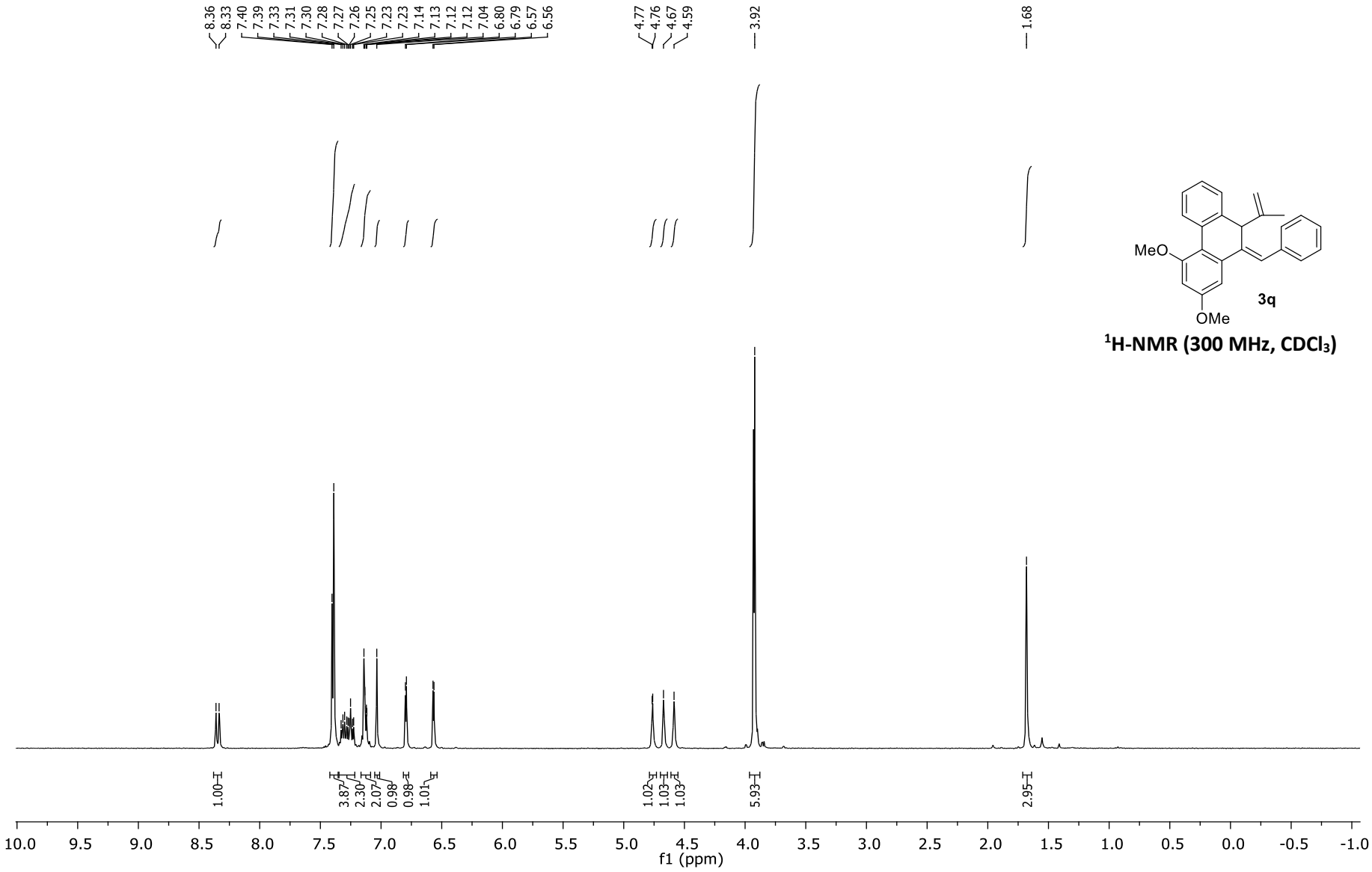


^{13}C-NMR (125 MHz, $CDCl_3$)

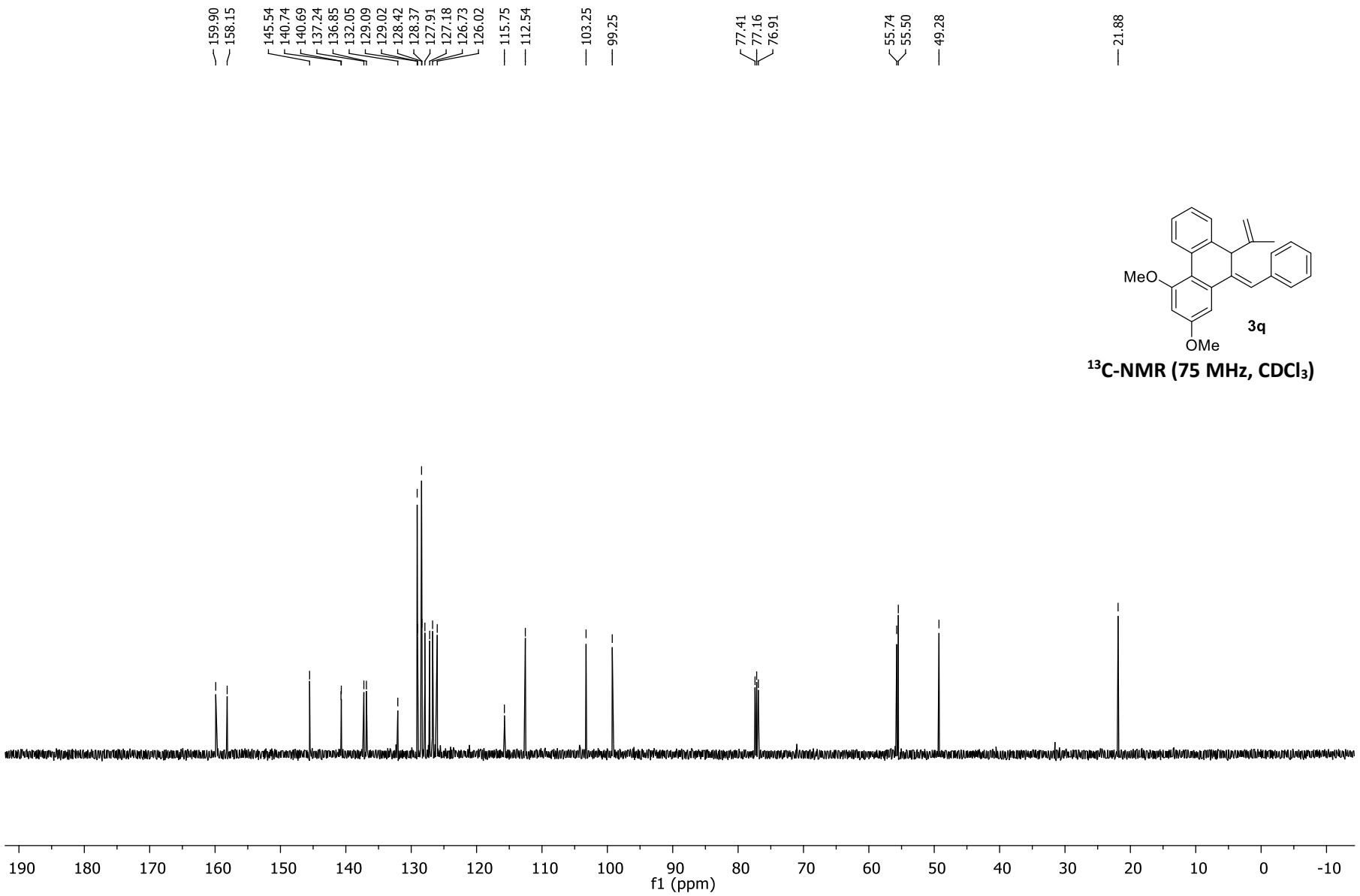


^{1}H-NMR (300 MHz, $CDCl_3$)

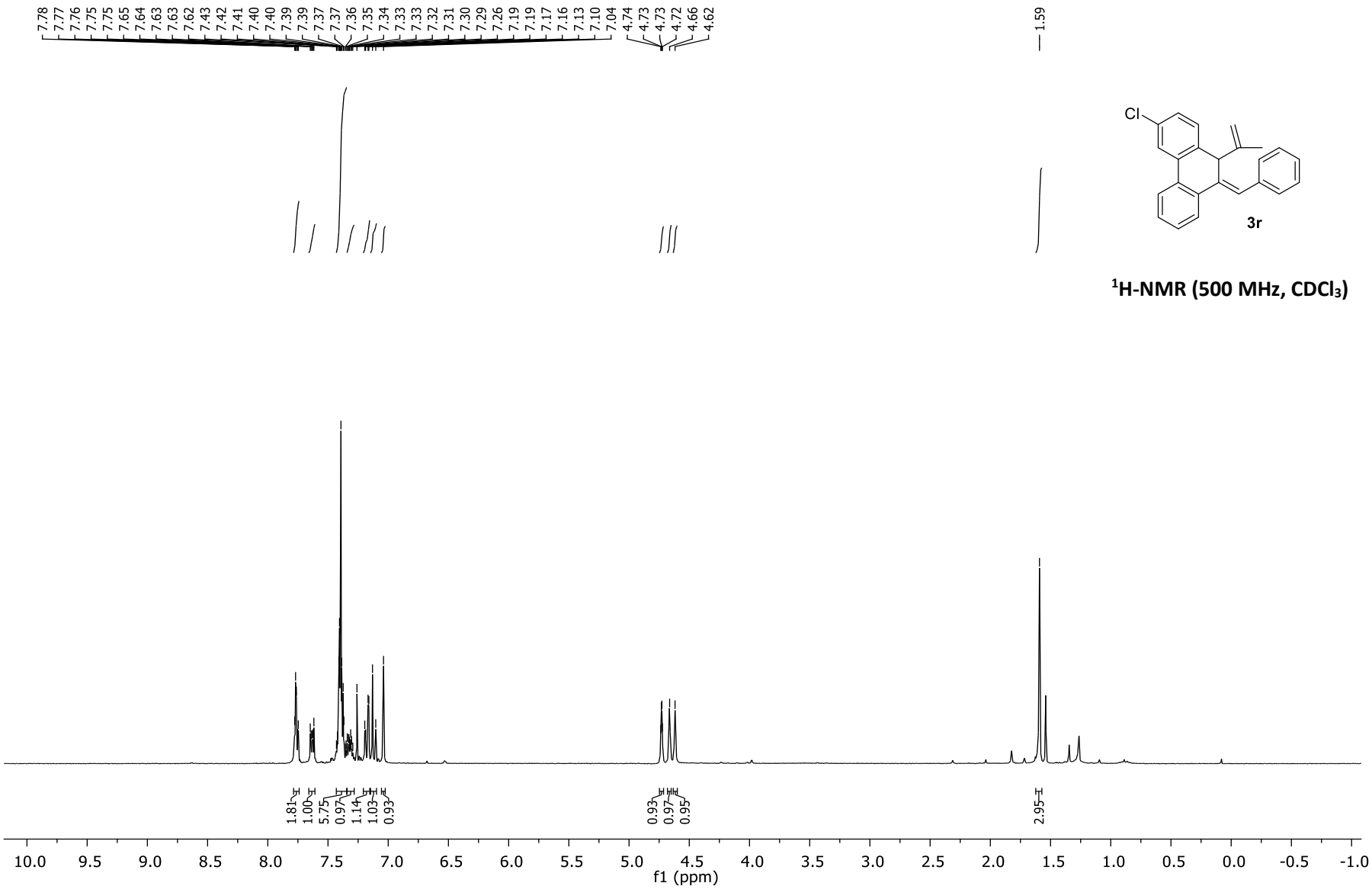

159.08
146.28
139.25
129.24
128.75
128.50
128.41
127.46
127.13
126.03
125.25
114.71
113.14
112.67
77.41
77.16
76.91
55.45
49.32
21.60
OMe
3p
^{13}C-NMR (125 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



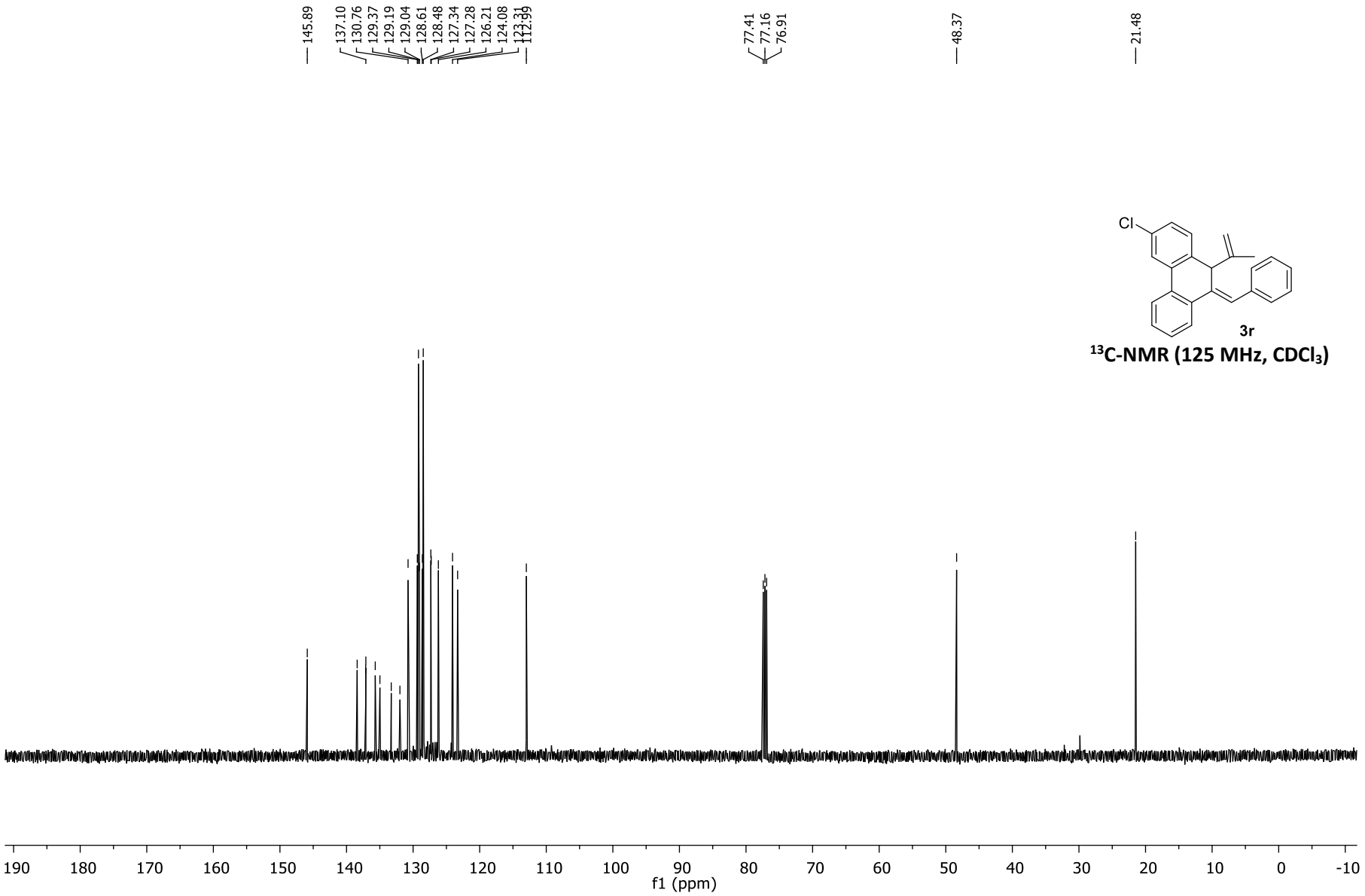
^{1}H-NMR (300 MHz, $CDCl_3$)

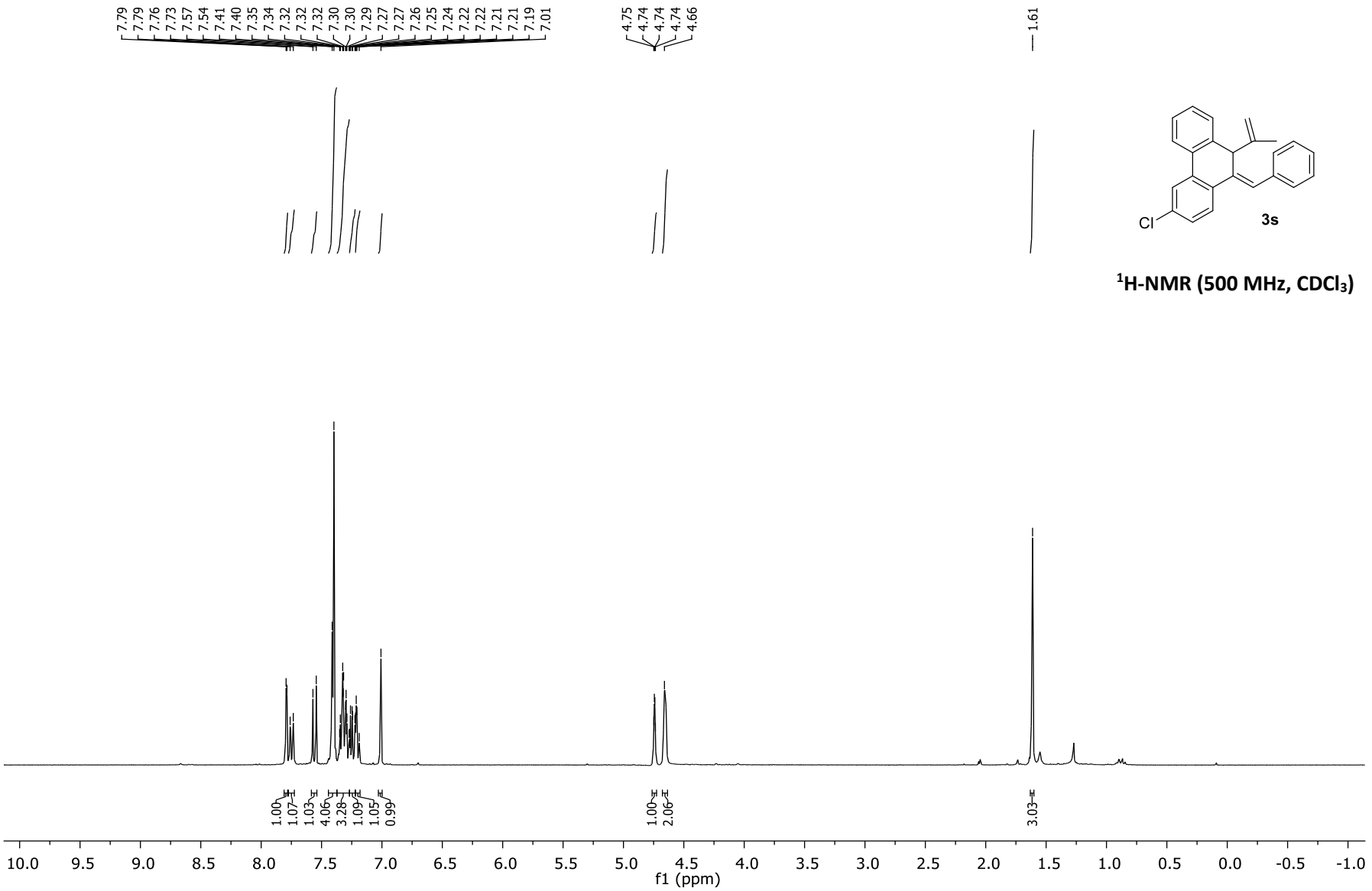


^{13}C-NMR (75 MHz, $CDCl_3$)

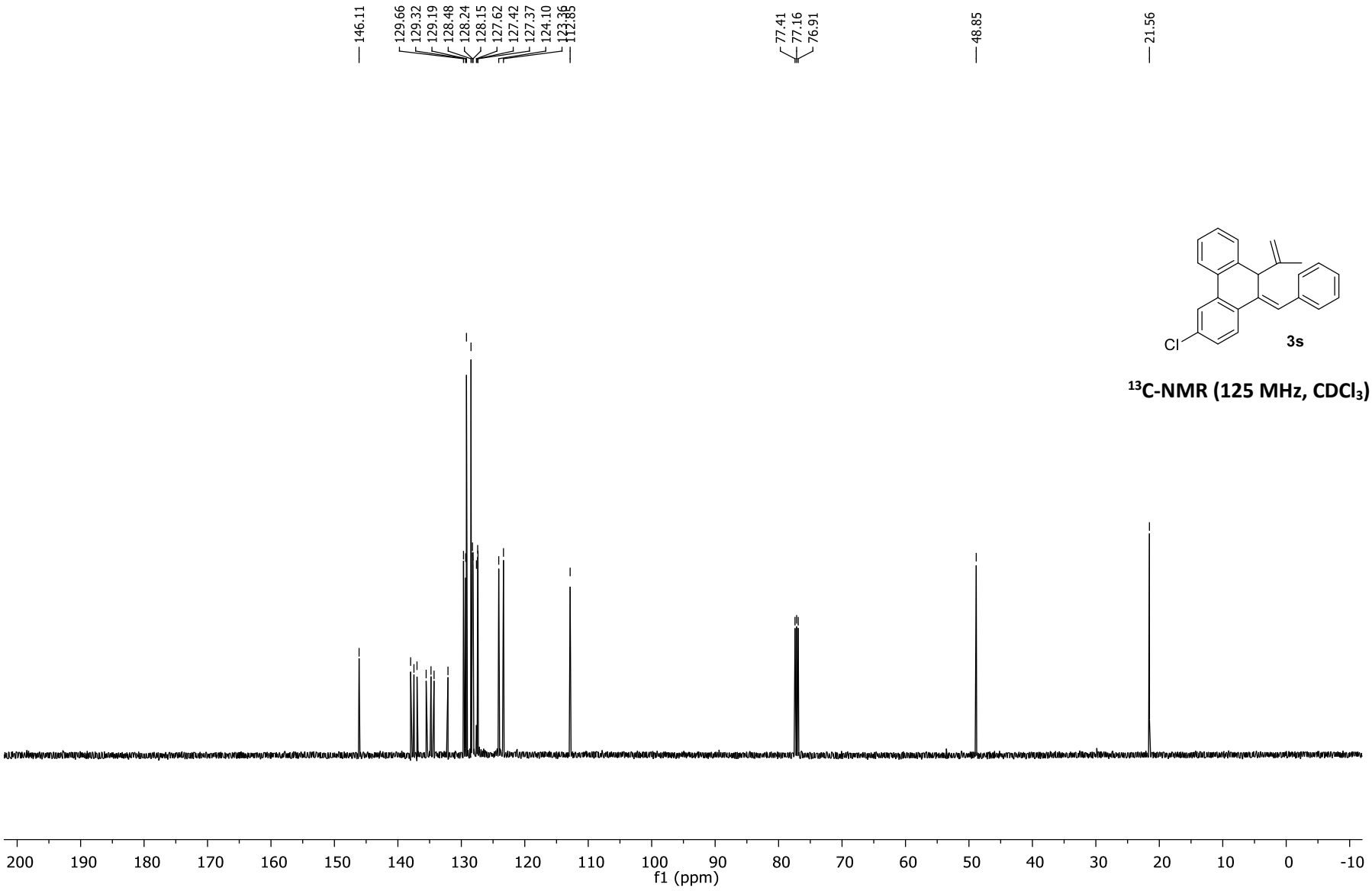


^{1}H-NMR (500 MHz, $CDCl_3$)


145.89
137.10
130.76
129.37
129.19
129.04
128.61
128.48
127.34
127.28
126.21
124.08
123.31
112.99
77.41
77.16
76.91
48.37
21.48
Cl
3r
^{13}C-NMR (125 MHz, CDCl$_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



^{1}H-NMR (500 MHz, $CDCl_3$)



^{13}C-NMR (125 MHz, $CDCl_3$)

Crystallographic data for 2a, 2b, 3q and 5t:

Colourless crystals of **2a**, **2b**, **3q** or **5t** were grown by slow evaporation at room temperature from a solution of the compound in a mixture of *n*-hexane and dichloromethane. The crystals were removed from the vial and covered with a layer of a viscous perfluoropolyether (FomblinY). Suitable crystals, selected with the aid of a microscope, were mounted on a cryoloop and placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for compounds **2a**, **2b**, **3q** and **5t** are presented in Table S3.

The structures were solved, using the WINGX package,[13] by intrinsic phasing methods (SHELXT)[14], and refined by least-squares against F^2 (SHELXL-2014/7).[15] In the crystallographic studies for all these compounds, all non-hydrogen atoms were anisotropically refined, whereas all the hydrogen atoms were positioned geometrically and refined by using a riding model.

[13] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849-854.
[14] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3-8.
[15] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.

Table S3. Experimental data for the X-ray diffraction study on compounds **2a**, **2b**, **3q** and **5t**

	2a	**2b**	**3q**	**5t**
formula	$C_{24}H_{20}$	$C_{25}H_{22}O$	$C_{26}H_{24}O_2$	$C_{23}H_{18}$
CCDC[a] code	2011662	2011663	2011664	2011665
M_r	308.40	338.42	368.45	294.37
T [K]	200	200	200	200
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$
a [Å]	10.080(3)	7.702(1)	12.171(1)	7.114(1)
b [Å]; β (°)	7.281(1); 90.45(1)	13.329(1)	12.240(1); 100.14(1)	11.592(1)
c [Å]	23.090(4)	18.063(2)	13.612(1)	19.595(3)
V [Å^3]	1694.5(6)	1854.4(3)	1996.2(3)	1615.9(3)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.209	1.212	1.226	1.210
$\mu_{MoK\alpha}$ [mm^{-1}]	0.068	0.072	0.076	0.068
F(000)	656	720	784	624
crystal size [mm^3]	0.18 × 0.15 × 0.14	0.30 × 0.28 × 0.26	0.41 × 0.39 × 0.36	0.35 × 0.25 × 0.20
θ range (deg)	3.31 to 27.50	3.06 to 27.50	2.98 to 27.50	3.05 to 27.48
index ranges	−12 to 13 −9 to 9 −30 to 29	−10 to 10 −17 to 16 −22 to 22	−15 to 15 −15 to 15 −17 to 17	−9 to 8 −14 to 14 −25 to 25
reflns collected	33885	23887	35549	20724
unique data	3893 [R(int) = 0.114]	4217 [R(int) = 0.043]	4574 [R(int) = 0.149]	3677 [R(int) = 0.047]
obsd data [$I > 2\sigma(I)$]	2069	3483	2433	3080
GOF on F^2	1.027	1.083	1.157	1.064
final R[b] indices [$I > 2\sigma(I)$]	R1 = 0.068 wR2 = 0.136	R1 = 0.040 wR2 = 0.084	R1 = 0.072 wR2 = 0.120	R1 = 0.042 wR2 = 0.084
R[b] indices (all data)	R1 = 0.154 wR2 = 0.168	R1 = 0.058 wR2 = 0.093	R1 = 0.172 wR2 = 0.160	R1 = 0.058 wR2 = 0.092
largest diff. peak/hole [e Å^{-3}]	0.247 and −0.188	0.161 and −0.179	0.239 and −0.317	0.141 and −0.198

[a] Cambridge Crystallographic Data Centre. [b] $R1 = \sum||F_0|-|F_c||/[\sum|F_0|]$; $wR2 = \{[\sum w(F_0^2 - F_c^2)^2]/[\sum w(F_0^2)^2$

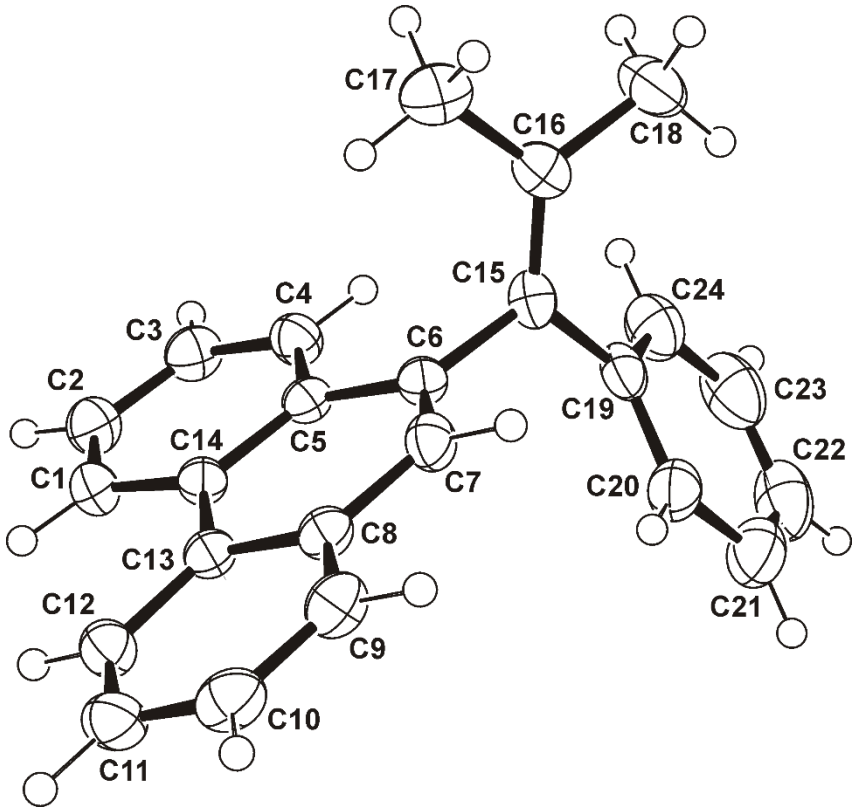


Figure S1. X-ray structure and numbering scheme for **2a**. Thermal ellipsoids are drawn at the 50% probability level.

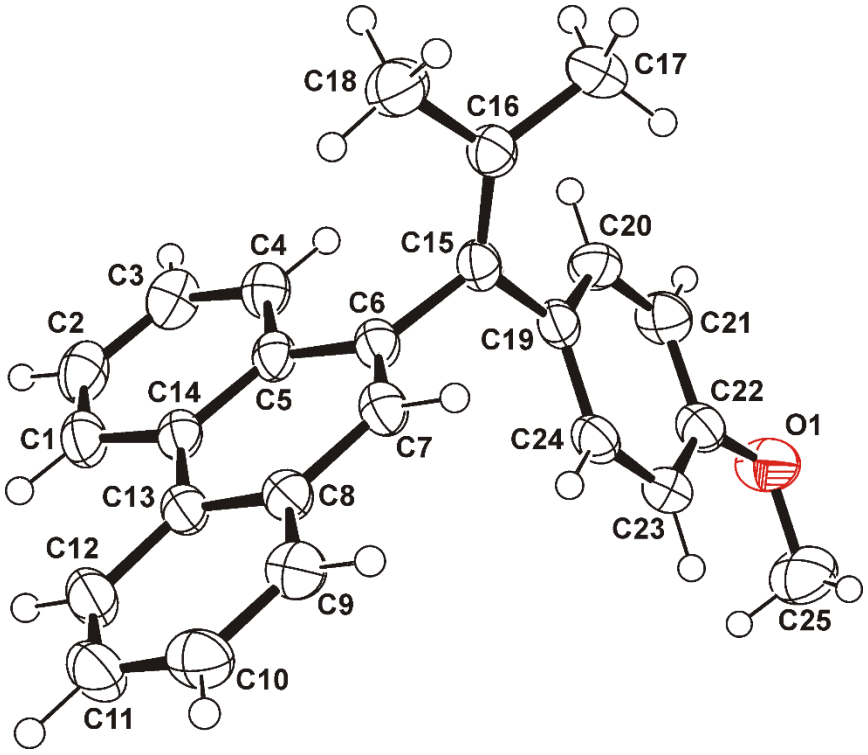


Figure S2. X-ray structure and numbering scheme for **2b**. Thermal ellipsoids are drawn at the 50% probability level.

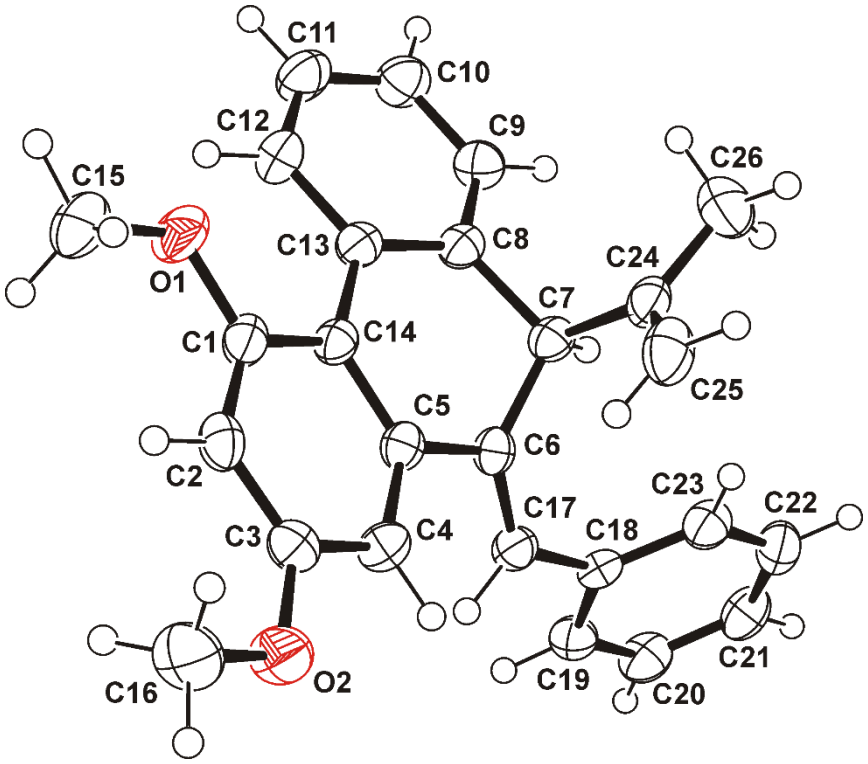


Figure S3. X-ray structure and numbering scheme for **3q**. Thermal ellipsoids are drawn at the 50% probability level.

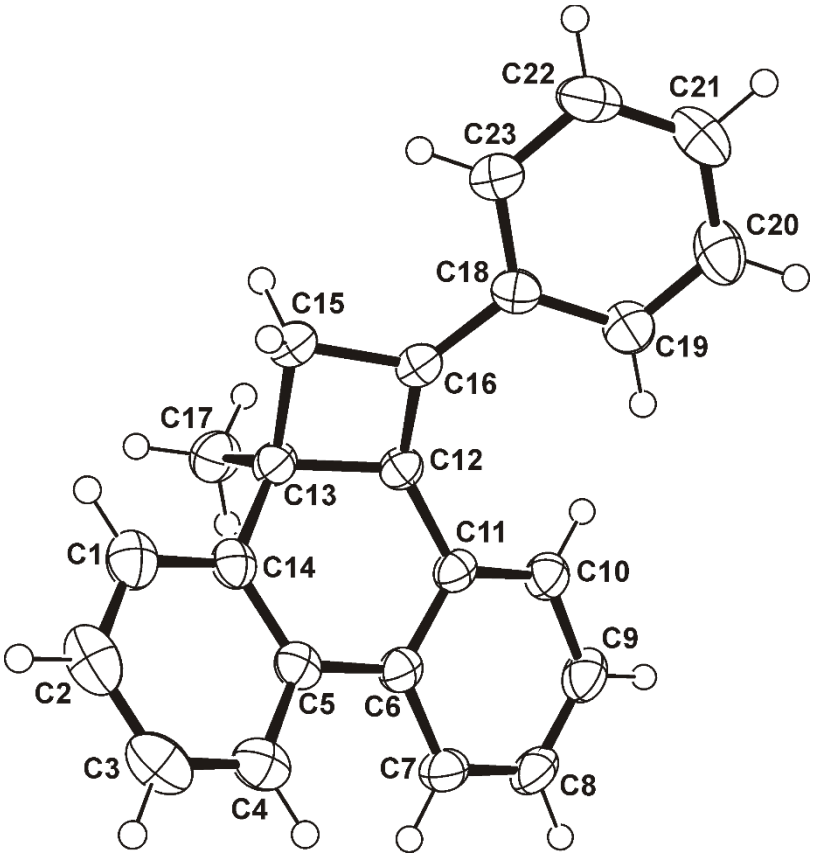


Figure S4. X-ray structure and numbering scheme for **5t**. Thermal ellipsoids are drawn at the 50% probability level.